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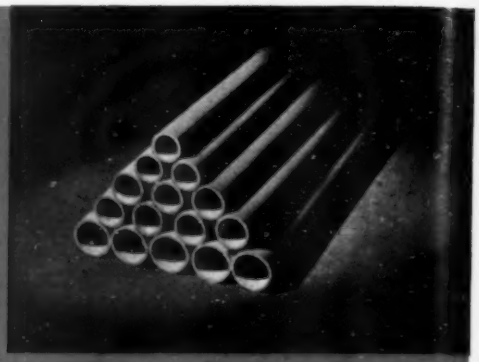

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METALLURGIA

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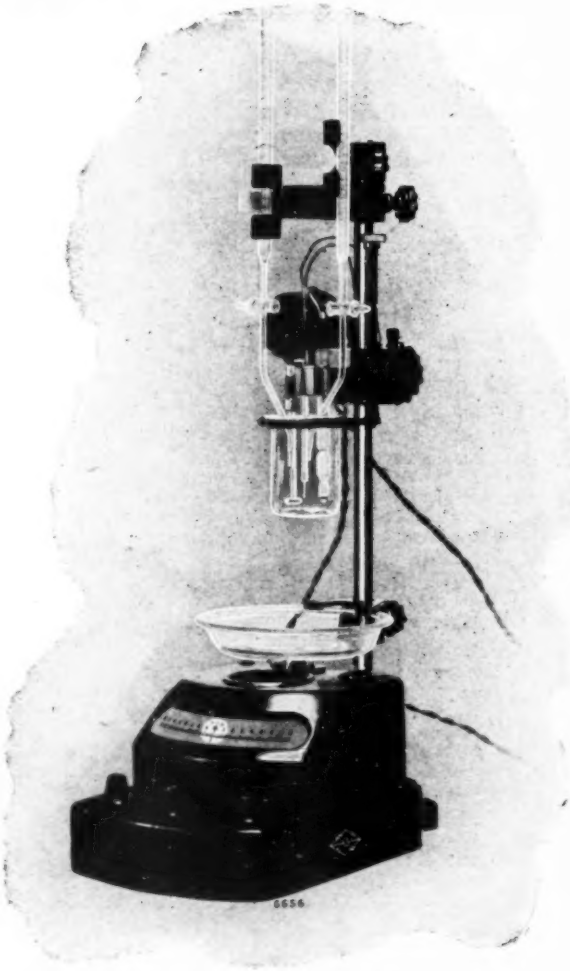

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METALLURGIA

THE BRITISH JOURNAL OF METALS.

INCORPORATING "THE METALLURGICAL ENGINEER."

FEBRUARY 1948 Vol. XXXVII No. 220

Direct Ore Reduction

THERE have been many fruitless attempts at by-passing the blast furnace as the means of ultimately producing steel from iron ore. The patent literature of most countries is strewn with descriptions of derelict processes of direct reduction—some untried, some unworkable, some uneconomic and many having had expended upon them huge sums for their development. All these processes foundered on a rock of impracticability. It is comparatively easy to prove on paper that a theoretically sound direct reduction process must be economical. After all, the operation is carried out which takes place in the shaft of the blast furnace and removes the product of low-temperature gaseous reduction before it gets to the bosh and the hearth. If this is done then the fuel consumption will be less than that required in the blast furnace. The sponge iron produced is ideal for steel production in open-hearth or electric furnaces.

Yet, in spite of the apparent metallurgical simplicity of this process, it is only in Sweden that sponge iron has been regularly manufactured on a profitable commercial scale. This has been due to a combination of factors—some economic, some technical. Some of these factors are discussed elsewhere in this issue by Dr. Tigerschiöld and Mr. Eketorp who have had considerable experience in the successful production of sponge iron, and who direct particular attention to economic aspects of its production and use.

Sweden is naturally endowed with certain important deposits of extremely pure iron ore—in particular, magnetites capable of concentration up to 71·5% metallic iron. This practically eliminates the gangue problems. Furthermore, fuel is expensive and a process of producing iron, with less carbonaceous fuel than the blast furnace, is far more attractive than in countries which have relatively cheap indigenous coking coal.

Sweden has also concentrated on producing a base for manufacturing high-grade tool and alloy steels and sold her sponge iron at a premium for these purposes, even in the export market. In this she has been assisted by the exceptional purity of the concentrates and the fact that the resulting sponge contains a small content of vanadium which enhances its value and produces a high-grade product.

In this country, Swedish sponge iron is being used to a limited extent for these special purposes both in arc and high-frequency furnaces, but the consumption can be measured in hundreds of tons only. Some half-hearted attempts have been made to operate direct processes here, but these have failed either through lack of capital or through over ambitiously treating ores containing far too much gangue. In Germany, the Krupp-Renn process was heralded as the solution of direct reduction and although it was made to operate under certain conditions, it was found to be riddled with practical difficulties.

In America, during the war, scrap shortage compelled the War Production Board to consider alternative sources of melting stock, and this problem was seriously investigated by the United States Bureau of Mines. A sponge-iron plant was built by Brassert at the Republic Steel Corporation's plant, using magnetite concentrates and the hydrogen in coke-oven gas as the reducing agent. This plant, though interesting as a technical development, never achieved full production and became redundant with the cessation of hostilities.

What then is the future for sponge iron as a method of producing steel? In spite of all the vicissitudes, it is a process which holds out considerable possibilities and this is, in no small measure, due to the changing world economic picture. The age of cheap coal, especially coking coal, has passed. Many countries can already see the end of their coking coal reserves. The iron ore reserves in the principal steel-making countries are decreasing in richness—the process of winning the richest ores first is taking its toll, with the result that large-scale processes of ore beneficiation have been developed with considerable success. One of these latter processes is the logical starting point for direct reduction—namely, fine grinding; a magnetising roast; concentration; followed by pelletising or glomulerising. This latter process is an interesting development inasmuch as it appears to be the most successful method of agglomerating for a furnace charge very fine material say—200 or 300 mesh. Providing there is an appreciable colloidal fraction, it can be moistened, balled up and the spheroids calcined in a recuperative shaft furnace producing an ideal porous reducible charge. What is more important is that this can be done under normal conditions at a lower cost than sintering, whilst it avoids the adulteration of the raw material with coke ash. These pellets can be readily reduced in a shaft furnace by hydrogen or carbon-monoxide, or mixtures of these.

These developments are the starting point of a process built on much surer foundations than any which have been tried in the past and found wanting.

The most obvious application for direct reduction is in those countries possessing adequate iron ore resources with a dearth or absence of coking coal, but with some other source of carbon or hydrogen such as non-coking coals, lignite or oil from which to generate a reducing gas. Such localities are found in India, Southern Africa and Australasia, as well as in Scandinavia and Italy. It is theoretically possible to produce steel by such methods, using only water power for electrolytic hydrogen and iron ore.

In this country serious consideration might be given to a plant for producing high-grade tool steel melting stock, some of which is now imported, but the day is not yet in sight when tonnage steel can be made by this

method in countries possessing still abundant supplies of coking coal. As the price of coal rises, the proposal to make sponge iron becomes more and more attractive as the amount of coal required as a reducing agent is less than one half of that used at present in the blast furnace.

Much development work on plant still requires to be done, but the experience of the countless abortive attempts to launch this steel-making process is beginning to bear fruit, and in recent years the efforts of Sieurin, Wiberg and Brassert have brought this process a long way along the road to becoming a serious consideration in any new project.

British Oilfield Equipment

SINCE the war British engineers have made considerable progress in the production of oilfield equipment. Before the war this highly specialised branch of engineering was largely in the hands of American engineers who had means at hand for testing new equipment and new techniques. It is true that several British firms were engaged in manufacturing items to the oil companies' specifications, but few were solely engaged on such work and the value of the work done only amounted to a few hundred thousand pounds annually. The position has changed considerably; last year, for instance, equipment valued at £47,000,000 was supplied to British oilfields and this year's orders to be satisfied are worth £71,000,000.

This progress, as pointed out in a recent address by Mr. G. L. Hancock, general manager of The David Brown Foundries Co., Ltd., has resulted from a concerted effort by British engineers to capture, at least, the market offered by British oilfield companies. The results so far have not only concerned British foreign exchange resources, but, by augmenting American sources of supply—strained by the first part of the U.S.A. two-year programme involving the expenditure of over $4,000 million—have made a contribution towards solving the world problem of maintaining adequate supplies of oil at a time of universal coal shortage.

It is estimated that, by 1951, the Near East and Persian Gulf producing areas may be exporting more oil than the whole of Latin America, and it is tempting to speculate what all this development means in terms of engines, power stations, pipelines, refineries and transports. But, at present, that must be mere speculation, for, despite the amazing performance of British engineers during the last two years, a gap remains between what Britain is able to supply over the next two years and what the oil industry requires. So far as 1948 is concerned the following figures give the supply and demand picture, the first figures representing the estimated capacity to supply and the figures in brackets the sum total of the oil companies' field requirements: Drilling equipment, £1,894,708 (£4,751,382); production equipment, £845,488 (£1,042,988); pumps, £910,428 (£1,110,428); instruments, etc., £823,750 (£1,009,000); valves and cocks, £1,742,070 (£1,930,820); packings and jointings, £192,501 (£226,001); petroleum dispensing equipment, £579,369 (£604,369); electrical equipment, £1,952,363 (£2,159,863). Examination of the demand for refinery plant shows a similar position. That gives the broad national outline of what the development of this new branch of engineering has meant during the last two years and what it will mean to the Commonwealth in the years ahead. Mention was made of more processing of oil in the United Kingdom; one new extension was referred to—viz., a refinery at North Shields, to cost £2,000,000, has recently been authorised as part of an immediate expenditure of £14,000,000 on such works.

Co-operation of manufacturers, to which the remarkable success of this new branch of British engineering is to a large extent due, is so complete that work is already going on with the oil companies in connection with standardisation under the ægis of the British Standards Institution, which will obviate innumerable supply difficulties.

Record Steel Production

A NEW monthly steel production record was established in January. Production was at the rate of 14,589,000 tons per annum, compared with 12,646,000 tons a year in December and 12,470,000 tons in January, 1947. The previous highest month's production was during October last year when the annual rate of 14,316,000 tons was reached, while the best previous January figure was in 1943 when production was at the annual rate of 12,927,000 tons.

Pig iron production also showed an increase to an annual rate of 8,726,000 tons compared with 8,561,000 tons in December and 7,806,000 tons in January, 1947. The detailed statistics of the British Iron and Steel Federation are as follows:—

PIG IRON IN TONS

	1946		1947	
	Weekly Average	Annual Rate	Weekly Average	Annual Rate
November	153,900	8,002,000	165,900	8,617,000
December	153,200	7,966,000	164,600	8,561,000
Fourth Quarter	154,400	8,029,000	163,600	8,505,000
	1947		1948	
January	150,100	7,806,000	167,800	8,726,000

STEEL INGOTS AND CASTINGS IN TONS

	1946		1947	
	Weekly Average	Annual Rate	Weekly Average	Annual Rate
November	263,800	13,715,000	272,600	14,174,000
December	236,300	12,289,000	243,200	12,646,000
Fourth Quarter	251,700	13,088,000	263,100	13,679,000
	1947		1948	
January	239,800	12,470,000	280,600	14,589,000

These figures are very encouraging and show that the iron and steel industry is doing its utmost to meet the increasing demand for more steel. It will be noted that the production rate during the month exceeds the steel target figure for 1948. However, records are made to be broken, and it is unlikely that this January record will remain for many months. But much depends upon the amount of scrap iron which will become available to the industry. The position is becoming very serious. All scrap iron and steel should be carefully garnered and collected by a reputable firm for re-use. There are few engineering works that could not make very substantial contributions to meet the present demand, and if only antiquated plant and machinery, which, in many cases, have been derelict for years, could be ruthlessly discarded, the amount of scrap to become available would rapidly remove present fears. A considerable amount of iron and steel scrap is expected from Germany and doubtless much army and navy equipment will augment supplies, but regular returns from works provide the basis upon which the industry largely depends. It is hoped, therefore that the consuming industries will assist the iron and steel industry to improve upon the record established.

The Use of Sponge Iron for Steel Production in Sweden*

By M. Tigerschiöld† and S. Eketorp‡

Much work has been carried out with the object of producing steel direct from ore instead of by the indirect blast-furnace process. Only in Sweden, however, has the process been successfully developed to a practical conclusion. Several sponge-iron methods have been developed, but so far the Höganäs and Wiberg methods are the only ones operating. In this paper the authors briefly review the main developments of the sponge-iron process and discuss the Höganäs and Wiberg methods, directing particular attention to the economic aspects of their application. Contributions to a discussion on the subject are also given.

IT is now generally realised, that the blast-furnace process was developed from more direct methods of making iron used in earlier days. This development proceeded as it became possible to build larger and higher furnaces in which temperatures could be attained sufficiently high to melt the iron. The modern blast furnace is certainly a very simple and economical reduction apparatus and its capacity for production is now increased to values which would have been unbelievable only a few decades ago. It is not surprising, therefore, that the steel industry to-day is based almost exclusively on the blast furnace.

From time to time, however, since the beginning of the 19th century, suggestions have been made and experiments carried out with a view to producing steel directly from ore, instead of by the roundabout method of first producing pig iron. In Sweden especially much thought and money have been spent with the object of carrying these ideas through to a practical conclusion.

As early as 1823 *Chenot* in France started working on a sponge-iron process, which in 1850 was used in the steel industry in quite a few places. His method, in which the ore was reduced directly and continuously in a clay crucible, did not prove to be very satisfactory, but it was of fundamental importance in the development of sponge-iron processes.[1, 6, 7]

The first sponge-iron process to be used in Sweden was that invented by *Sieurin*[2, 3] at Höganäs 1908. This method has been in use on an industrial scale since 1911 and it seems perhaps strange that this method has not been more widely developed and used in other steel-producing countries. The reason is that this process was not generally thought to be economical, except where very cheap fuel was available and where facilities were available to produce the clay containers, which are consumed in large quantities. The Höganäs Company has been more interested in selling its sponge iron in limited quantities at higher prices rather than in building a new and modern factory where the sponge iron could be produced at a low cost. During recent years, however, the method has been systematically improved, and it now seems that there are possibilities for a more general use of this process. In the United States some rather extensive experiments with this type of process have been carried out at the Bureau of Mines,[14, 15, 16] in order to determine some of the unknown details of the method.

Wiberg in 1918 invented his sponge-iron process, which is based on gas reduction.[4] Circulation of the gas in this process makes possible full utilisation of the gas for reduction and a low consumption of coal and power can be obtained. At that time it was certainly not believed that his figures for coal and power consumption would hold, when applying the process in practice. It has since been shown, however, that they were not too optimistic and in fact they have been surpassed in the plant now in operation.

Apart from these two processes there are others which should have possibilities of being developed economically, for instance, those of Kalling and Norsk Staal; but as yet the Höganäs and Wiberg methods are the only ones operating.

In the United States, as well as in other countries, the sponge-iron problem has always been of current interest and subject to many investigations and experiments. Thus far, however, no process has been developed, in spite of the fact that millions of dollars have been spent on experimental work. Although no practical results have been achieved this work has been of great importance in obtaining a more thorough knowledge of the sponge-iron problem. Certainly the U.S. Bureau of Mines method of producing sponge iron in a rotary kiln is of exceptional interest. The work now carried on with hydrogen as a reducing agent also might lead to an interesting solution of the problem, at least in places where no fuel is available and hydro-electric power is cheap.

In Sweden fuel is expensive and the main problem of the steel-making processes in many instances is a fuel problem. Hence, a sponge-iron process must be efficient in fuel consumption. This condition holds for both of the Swedish methods mentioned.

During the last 20 years in Sweden there has been much discussion of the possibilities of introducing the sponge iron on a larger scale in Swedish steel industry, because of the shortage and high cost of charcoal pig iron and of high-grade scrap.[5, 6, 7, 10] During this time the Wiberg method came into use at the tool steel plant of Söderfors[8] and now the second plant employing this method is under construction in Sandviken. The interest in the Höganäs method has been increased by the publication of more data on the process[9] and two years ago the

* Translated and abstracted from a paper in Swedish by *M. Tigerschiöld*[11] together with some notes from a lecture on sponge iron by *S. Eketorp* held in Sheffield, October, 1947.

† Director of Research, Jernkontoret, Sweden.

‡ Superintendent, Höganäs Sponge Iron Works, Sweden.

Höganäs Company invited all the steelworks to a discussion of the possibility of building a common sponge-iron plant in the middle of the steel industry district in Sweden.

Thus, it can be seen that the interest in sponge iron is rapidly growing. As a part of the activities of Jernkontoret (The Swedish Ironmasters' Association) a committee was set up to investigate the possibilities of using more sponge iron for steel production. Many of the data published in this paper are based on the work of this committee.*

Calculations of the Composition of Sponge Iron Using Different Raw Material

In the Höganäs process it has been customary to use an iron concentrate from ore with the highest possible content of iron. This ore is a magnetite from the northern part of Sweden containing 71·5% Fe, low in phosphorus and sulphur. One of the advantages of this process is that the degree of reduction is high, usually about 96%.

In the other process working at Söderfors a sinter with 60% has mainly been used. It has been found, however, that it is more favourable to work with a concentrate with 65% Fe and it is intended to switch over to this concentrate within a short time. With this iron content it is most convenient to work with a degree of reduction of 90% and experiments have shown that when using concentrate with 71·5% it is possible to obtain 93% reduction.

TABLE I.—ORE ANALYSES

Raw Material	Concentrate with 71·5% Fe			Concentrate with 65% Fe			Lump Ore (Striberg Hematite)
	Conc.	Normal Sinter	Pellets	Conc.	Normal Sinter	Pellets	
Fe	71·5	68·64	69·14	65·0	62·59	63·04	46·30
Fe_3O_4	98·81	—	—	89·85	—	—	—
Fe_2O_3	—	98·14	98·85	—	89·49	90·13	66·20
O : Fe-oxides	27·31	29·50	29·71	24·85	26·99	27·09	19·90
Gangue	1·19	1·86	1·15	10·15	10·51	9·87	33·80

Table I shows analyses for some ores and the sinter produced from them. The two separate analyses of the latter are calculated, one for the use of the normal sintering process and the other for the new pelletizing process. This latter method, which was patented in Sweden[11] as early as 1912, is now under intensive study in the United States and also in Sweden. One of the advantages of this process is that the combustion can be carried out with gas and consequently no contamination from coke-ash will occur.

TABLE II.—SPONGE IRON ANALYSES, ETC.

Raw Material	Concentrate with 71·5% Fe			Concentrate with 65% Fe			Lump Ore (Striberg Hematite) 46·30% Fe
	Conc.	Normal Sinter	Pellets	Conc.	Normal Sinter	Pellets	
Deg. of red. %	96	93	93	96	90	90	90·27
Fe_{tot} %	97·27	95·50	96·47	85·62	83·57	84·38	56·50
Fe_{met} %	93·38	88·81	89·71	82·20	75·22	75·94	51·00
FeO %	5·09	8·62	8·71	4·40	10·73	10·87	7·09
O_2 %	1·11	1·92	1·94	0·98	2·39	2·42	1·58
Gangue %	1·62	2·58	1·59	13·40	14·04	13·20	41·92
Required/ton sponge:							
Sinter kg	—	1391	1395	—	1336	1338	—
Concentrate Sinter 1·02 kg	—	1419	1423	—	1363	1365	—
Lump Ore kg							1220
Removed O_2 kg/ton sponge	360	391	395	317	336	338	220

* Dr. M. Tigerschiöld was Chairman of this Committee.

With normal sintering, with coke consumption of 5%, the percentage of gangue in the sinter will increase by 0·75% due to the coke-ash. Highest possible degree of oxidation, which is attained in normal practice in Sweden, is calculated for both of the sintering processes. Table I shows also the analysis of a lump ore, a quartzose hematite from Striberg, on which some interesting experiments have been made.

When calculating the analysis of sponge iron from different raw material the equations 1–8 are valid, numbers 1–4 for magnetite, numbers 5–8 when hematite or sinter is the raw material.

Sponge-iron analyses for the ores in Table I are shown in Table II for various degrees of reduction. This table also shows the weight of concentrate, sinter and lump ore and the amount of oxygen removed.

*Composition of sponge iron made of magnetite ore (Fe_3O_4) · Fe — content in the ore = F %, degree of reduction of sponge iron = R %.**

$$(1)\quad Fe_{tot} = \frac{7236 \cdot F}{7236 - F\,(0{\cdot}2073 \cdot R + 6{\cdot}91)}\ \%$$

$$(2)\quad Fe_{met} = \frac{72{\cdot}36 \cdot F \cdot R}{7236 - F\,(0{\cdot}2073 \cdot R + 6{\cdot}91)} = \frac{Fe_{tot} \cdot R}{100}\ \%$$

$$(3)\quad O_2 = \frac{20{\cdot}73 \cdot (100\text{–}R) \cdot F}{7236 - F\,(0{\cdot}2073 \cdot R + 6{\cdot}91)} = (Fe_{tot}\text{–}Fe_{met})\,0{\cdot}2865\%$$

$$(4)\quad Gangue = \frac{(7236 - 100\,F) \cdot 100}{7236 - F(0 \cdot 2073 \cdot R + 6{\cdot}91)} = 100\text{–}(Fe_{tot} + O_2)\ \%$$

*Composition of sponge iron made of hematite ore (Fe_2O_3) · Fe — content in the ore = F^1 %, degree of reduction of sponge iron = R %.**

$$(5)\quad Fe_{tot} = \frac{6994 \cdot F^1}{6994 - F^1\,(0{\cdot}2004 \cdot R + 10{\cdot}02)}\ \%$$

$$(6)\quad Fe_{met} = \frac{69{\cdot}94 \cdot F^1}{6994 - F^1\,(0{\cdot}2004 \cdot R + 10{\cdot}02)} = \frac{Fe_{tot} \cdot R}{100}\ \%$$

$$(7)\quad O_1 = \frac{20{\cdot}02 \cdot (100\text{–}R) \cdot F^1}{6994 - F^1\,(0{\cdot}2004 \cdot R + 10{\cdot}02)} = (Fe_{tot}\text{–}Fe_{met}) \cdot 0{\cdot}2865\%$$

$$(8)\quad Gangue = \frac{(6994 - 100 \cdot F^1) \cdot 100}{6994 - F^1\,(0{\cdot}2004 \cdot R + 10{\cdot}02)} = 100\text{–}(Fe_{tot} + O_2)\ \%$$

The degree of reduction is defined as the ratio of metallic Fe to total Fe and thus equal to zero at a composition corresponding to pure FeO. For Fe_3O_4 it is equal to — 33·3% and for Fe_2O_3 equal to — 50·0%.

* When calculating these equations the atomic weight is taken as 55·84 for Fe and as 16·00 for O. The compositions for the various Fe-oxides is thus:

Fe_2O_3	Fe = 69·94%	O = 30·06%
Fe_3O_4	Fe = 72·36%	O = 27·64%
FeO	Fe = 77·73%	O = 22·27%

Of interest are the diagrams in Fig. 1 for magnetite concentrate and sinter or hematite ore, where the sponge iron composition is plotted against various iron contents of the raw material and at different degrees of reduction. From these diagrams it can be clearly seen how fast the gangue content increases with decreasing iron content in the concentrate.

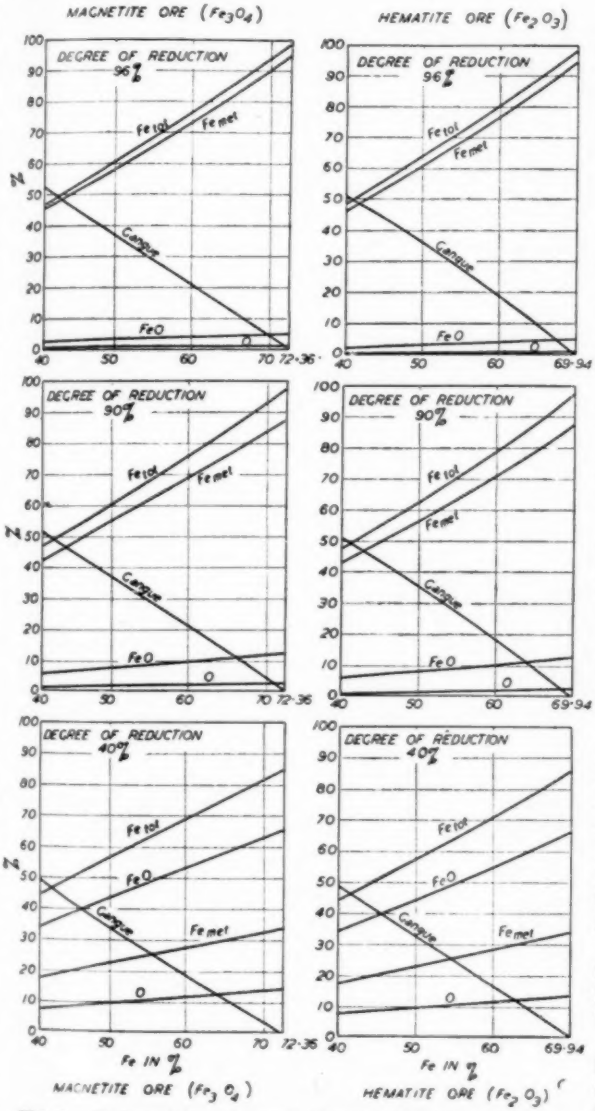

Fig. 1.—Composition of sponge iron at different degrees of reduction made with ores of different iron contents.

No consideration is given in these graphs to the fact that a certain amount of carbon absorbtion occurs in sponge iron processes. In the Höganäs process the carbon content of the sponge is usually below 0·10%, while the sponge iron in Wiberg process can take up about 1·7% C.

Production Costs of Sponge Iron

Wiberg process.—This method has been described in great detail by Améen[8] and on the basis of his paper and the excellent work done at Söderfors it is possible to carry out quite reliable calculations of production costs for this type of sponge iron. These calculations have been made for two sintered magnetite concentrates with 71·5% and 65% Fe and with varying degrees of reduction. A certain loss of iron is unavoidable and this loss has been assumed to be 2% occurring during sintering.

The calculations throughout this paper are based on an assumed production of 20,000 metric tons* per year. The essential function of the furnace is to remove oxygen from the ore and it seems, therefore, justifiable to assume that the power and coal consumption are directly proportional to the amount of oxygen removed per ton of sponge iron. The same holds true for the consumption of electrodes, lime for sulphur removal and for motive power. The cost for various materials, maintenance, refractories, labour and overhead, on the other hand, are given an assumed constant value. The variations in the item interest and amortization are derived as follows. The cost of construction would, of course, be less when reducing 20,000 ton sponge iron with low iron content than if the iron content was higher. Half of the cost of construction is supposed to vary in proportion to the oxygen removed, while the other part (buildings, foundations, etc.), are given an assumed constant value. The total amount for interest and amortization is fixed at 7·4%. All the costs given are for 1 ton of sponge iron. A total figure is also given per ton total Fe in the sponge.

When reducing sinter with 60% Fe the power consumption, according to Améen, is 850 kWh/ton and the coke consumption 200 kg. per ton of Fe in the sponge. If converted this will be 702 kWh/ton and 165 kg., respectively, per ton of sponge iron. The amount of oxygen removed will here be 326·7 kg. per ton sponge. With this relationship the other figures for power and coal have been calculated for the various alternatives.

In Table III the complete calculation of cost is summarised. The cost of sintering is 15s. 7d. per ton of sinter from concentrate with 65% Fe. The figure for the concentrate containing 71·5% Fe is 17s. 1d. per ton of sinter since this concentrate is richer and therefore more difficult to sinter. This sintering cost includes labour as well as interest and amortization (7·4%) of the sintering plant. The corresponding figures for pellitizing 7s. 9d. per ton, are supposed to be half the cost of normal sintering.

Labour force for the sponge-iron plant is 11 men. A sintering plant producing 30,000 tons a year should need 2 men per shift and 2 day-workers and accordingly the total labour force for the entire plant should be 19 men.

In all calculations coke is assumed to be the fuel. As is well known the plant at Söderfors up till now has been operating with charcoal, but successful experiments with mixtures of coke and charcoal, together with sulphur removal of the reducing gas with lime, have been carried out. It seems, therefore, to be safe to anticipate the advantage and better economy which coke will bring to this process. A carburettor for coke is now being installed and dependable results as to the possibilities of producing low sulphur sponge iron with coke will certainly be forthcoming very soon.

The sponge-iron plant is assumed to be located close to the mine, therefore, no freight is added to the cost of

* Note: All figures for weight in this paper are given in *metric tons* or *kilograms* (kg.). 1,000 kg. = 1 metric ton = 2,205 lb. = 0·984 tons, 1 lb. = 0·4536 kg. All cost figures are given in shillings and are based on an exchange of £1 = 14·50 Swedish kronor. 1 Swedish kronor = 1·38 shillings (November, 1947).

TABLE III.—PRODUCTION COST OF WIBERG SPONG IRON (SODERFORS)
(Production 20,000 ton per year)

Fe-content in the ore %	71·5				65·0			
Degree of reduction, sponge %	93·0				90·0			
Fe-content in sponge %	95·50		96·47		83·57		84·38	
Raw material for the reduction	Normal sinter amount	sh.	Pellets amount	sh.	Normal sinter amount	sh.	Pellets amount	sh.
Concentrate, 71·5% Fe, 40/- per ton	1419	56/9	1423	56/11	—	—	—	—
,, 65 % Fe, 27/7 per ton	—	—	—	—	1363	37/7	1365	37/8
Sintering, 17/1 per ton	1391	23/9	—	—	—	—	—	—
,, 15/7 per ton	—	—	—	—	1336	20/10	—	—
Pelletizing, 7/9 per ton	—	—	1395	10/10	—	—	1358	10/5
Coke, 138/- per ton	197	27/2	199	27/5	170	23/6	170	23/6
Lime, 31/9 per ton	50	1/7	50	1/7	43	1/4	43	1/4
Power, carburettor, 27/7 per 1,000 kWh	839	23/2	848	23/5	721	19/11	726	20/-
,, motive, 34/6 per 1,000 kWh	—	1/8	—	1/8	—	1/5	—	1/5
Electrodes, 8·3 d/kg.	3·5	2/5	3·5	2/5	3·0	2/1	3·0	2/1
Labour, 11 men—£345 per year	—	3/9	—	3/9	—	3 /9	—	3/9
Various material, maintenance	—	9/-	—	9/-	—	9/-	—	9/-
Overhead	—	9/9	—	9/9	—	9/9	—	9/9
Interest and amortization, 7·4 of £151,724	—	11/3	—	11/3	—	—	—	—
Interest and amortization, 7·4% of £140,000	—	—	—	—	—	10/4	—	10/4
Patent licence (assumed)	—	4/-	—	4/-	—	3/6	—	3/6
Shillings per ton of sponge iron	—	174/3	—	162/-	—	143/-	—	132/9
Shillings per ton of Fe in sponge iron	—	182/5	—	167/-	—	170/10	—	159/5

the ore. The costs given for the two concentrates containing 71·5 and 65% Fe, 40s. and 27s. 7d., respectively, are quite normal for a mine in the Swedish steel district. The cost of coke is set at 138s. per ton and the power at 27s. 7d. per 1,000 kWh for the carburettor and at 34s. 6d. per 1,000 kWh for motive power. The electrodes in the carburettor are of the Söderberg type and the cost for them is assumed to be 8·3d./kg. (3·8d./lb.). The labour costs per worker per year are assumed to be £345 in these calculations. Finally, the lime for cleaning the gas is set at 31s. 9d. per ton of lime.

As can be seen from table III, the cost of sponge iron varies considerably when it is made from various raw materials. If the cost of pelletizing is correct it would mean that the production cost of sponge iron could be reduced to between 11s. 1d. and 12s. 5d. per ton.

Concentration of Sponge Iron with Low Iron Content.—This problem has been investigated and discussed several times.[12, 13] Quite recently some new experiments have been carried out in connection with a small quantity of hematite ore from Striberg reduced at Söderfors. The analyses of the ore and the sponge are shown in Table I and II. After developing a new method of crushing an iron recovery of 92% has been obtained in the concentration, which was a wet process.

In order to obtain a good iron recovery it seems to be best to produce two products in the concentration, which later could be mixed. According to information given, these products have the following composition :

%	Low Grade Sponge	High Grade Sponge	Mixture
Amount	75	25	100
Degree of reduction	90	89·84	89·96
Fetot	85	93·5	87·13
Femet	76·5	84	78·38
FeO	10·94	12·22	11·26
O	2·44	2·72	2·51
Gangue	12·56	3·78	10·36

The cost of this concentration is calculated at 8s. 3d. per ton of end product plus drying cost of 2s. 7d. per ton. Consumption of raw sponge iron per ton of concentrated sponge will be :

$$\frac{1{,}000 \cdot 0{\cdot}8713}{0{\cdot}565 \cdot 0{\cdot}92} = 1{\cdot}676 \text{ kg.}$$

The reduction and concentration of this sponge iron has been carried out with a rather small quantity and a reliable calculation of production cost can therefore not be given. It seems, however, possible that the sponge iron produced in this way will be nearly as cheap as when concentrates higher in iron are used.

It should be possible to melt this material in the electric arc furnace without briquetting it. If this sponge is going to be used in acid open hearth or in high-frequency furnaces it is likely that briquetting will be needed. The cost for this is calculated to be 6s. 11d. per ton.

The Höganäs Process.—Unfortunately no detailed cost calculations are available for this type of sponge iron. It has, however, been stated officially by the Höganäs Company that according to their ideas it should be possible to produce this type of sponge iron at the same cost as by the Wiberg process at a new plant close to the ore, when a rich ore is used and when to-day's costs of coal and coke are valid.

Table II shows the analyses of Höganäs sponge iron from concentrate with 71·5% Fe. Ar 96% degree of reduction the iron content is as high as 97·27%, while the Wiberg sponge iron with normal sintering from the same raw material will run 95·5% Fe. According to Table III the cost for this sponge iron will be 174s. 3d. per ton. The cost of Höganäs sponge iron will be 177s. 6d., if the Company's report is correct.

Earlier Melting Practice of Sponge Iron

Höganäs sponge iron has been used since 1911 in the production of acid open-hearth steel. The Sandviken steelworks which have the greatest experience with sponge iron in Sweden, have used it as a regular addition in the charge for many years. No trouble has been experienced from corrosion of the furnace linings. For many years they worked with 12 to 13% in the charge, but during the last years have raised this to 15 to 20% Certain types, without trouble, carry 25% sponge iron in the charge of acid open-hearth steel.

The sponge iron is charged as follows : Pig iron is charged at the bottom of the furnace. When the pig iron is somewhat melted at the furnace ends the sponge iron is added. On the top of the sponge iron scrap is charged covering the sponge. If it is desired to keep the carbon content of the charge constant, 500 kg. of pig iron is added together with each ton of sponge iron in

order to prevent the sponge iron from decarburizing the charge too much. As can be seen the sponge iron in the acid open hearth is used as a substitute for domestic scrap.

Höganäs sponge iron is also quite regularly used in basic electric steel making. As the pig-iron percentage in the charge is usually rather low in making this steel, it is very valuable to have access to a pure virgin metal additional to the normal amount of circulating scrap. Both Sandviken and Bofors use Höganäs sponge iron when making their best qualities of electric steel, especially the unalloyed types. There are no difficulties whatever in melting a sponge iron of this well reduced and rich type in the basic electric furnace.

More than half of all sponge iron used in Sandviken is consumed in arc furnaces, the sponge iron replaces high quality scrap up to 70 to 80% in the charge. In these furnaces the sponge iron is added after charging pig iron and scrap at the bottom of the furnace. The sponge iron is considered to have a negative carbon content of 1% when calculating the charge.

At Stridsberg and Biörck, a small quality steel plant in Sweden, all steel is made with 30% sponge iron in an acid Rennerfelt furnace.

Sponge iron is also used in high-frequency furnaces with up to 45% in the charge as unbriquetted Höganäs sponge iron and 100% being used when briquettes of the same type of sponge are charged.

Melting of Sponge Iron and Cost Calculations for Steel Made from Sponge Iron

A. Basic electric arc furnace.—Améen publishes in his paper[8] complete information on methods of melting sponge iron in the basic electric arc furnace as developed in Söderfors. The granular sponge iron is there being charged through a hole in the roof of the furnace. Extra additions are made at regular intervals until the desired quantity is charged. In certain cases pig iron and scrap are added, these being melted before adding the sponge iron. In other cases extra charcoal is charged as a reducing agent mixed with the sponge. Before melting all the sponge iron the furnace is tilted in order to allow the slag produced to flow out of the furnace. Iron content in the slag normally is 7%. Generally no lime for fluxing the gangue is added in spite of the acid nature of the gangue in the concentrates used. If the concentrates, however, are very acid, some lime, of course, should be charged together with the sponge.

Assuming that the iron content in the slag is 7% independent of the gangue and the degree of reduction, it is rather easy to calculate the amount of sponge iron needed per ton of steel, together with the consumption of charcoal briquettes and the power for reduction of remaining iron oxides and melting of the gangue. When setting up the following equations it is further assumed that 1,050 kg. Fe per ton of ingot is consumed when making ordinary electric steel from pig iron and scrap. It is finally assumed that the steel produced will hold 0·5% C and that the charcoal briquettes analyse 85% C and 2% ash. The efficiency of the extra power for reduction and melting of slag is assumed to be 85%.

The reduction of FeO with carbon is assumed to occur according to the following equation :

$$11\ FeO + 10\ C = 11\ Fe + CO_2 + 9\ CO - 374{\cdot}9\ \text{cal.}$$

The reduction gases are assumed to leave the furnace at 700° C. The power consumption per kg. O will, therefore, be :

$2{\cdot}476 + 0{\cdot}345 = 2{,}821$ kWh per kg. O.

As the slag is supposed to be tapped off continuously at a rather low temperature it has been assumed that the thermal capacity is as low as 450 cal. = 0·52 kWh per kg. of slag.

If the total iron content of the sponge iron is termed F_s, the unreduced oxygen as O_s, and the gangue content as G and all these units are expressed in percentage, the following equations can be set up :

Amount of slag obtained :

$$(9)\quad S_l = 11 \cdot G + 0{\cdot}16 \cdot O_s + \frac{117{\cdot}64}{S_p}\ \text{kg. per ton of sponge.}$$

Extra amount of power required :

$$(10)\quad P = 33{\cdot}27 \cdot O_s + 6{\cdot}00 \cdot G + \frac{72{\cdot}00}{S_p}\ \text{kWh per ton of sponge.}$$

Amounted of reducing agent, briquettes of charcoal, required :

$$(11)\quad R = 8{\cdot}02 \cdot O_s - 0{\cdot}176 \cdot G + \frac{5882}{S_p}\ \text{kg. per ton of sponge.}$$

In order to produce 1,000 kg. o fsteel by melting sponge iron only :

$$(12)\quad S_p = \frac{1{,}050 \cdot 1{,}000}{10 \cdot F_s - 0{\cdot}77 \cdot G}\ \text{kg. sponge per ton of steel is needed.}$$

The last terms in equations 9 and 10 could, in most cases, be neglected. They represent power consumption for the melting of charcoal ash. When deriving the equations the iron content of the slag is assumed to be 7%. When this content is increased to for instance 10%, the result will be essentially the same especially if sponge iron with little gangue is used.

In Table IV the values are summarised for consumption of sponge iron, the amount of slag formed and charcoal needed for reduction. Different types of sponge iron are listed. Table V shows the production cost of electric steel when calculated on the basis of the data from Table IV. When calculating the production cost for ordinary electric steel the pig iron percentage in the charge is set at 20%, the percentage of domestic scrap at 30% and purchased scrap of good quality at 50%. The amount of domestic scrap is held constant for all alternatives at a cost of 207s. per ton, while pig iron as well as purchased scrap is set at 276s. per ton. The charges with sponge iron all consist of 70% sponge and 30% domestic scrap. The price of this last type of scrap is set constant at 207s. per ton because of the impossibility otherwise to obtain comparable figures for production cost per ton of finished rolled steel. The cost for domestic scrap should more properly be zero as it is circulating in the process. The figure 207s., however, is chosen in order to obtain ingot costs corresponding to practical conditions.

Consumption of power for making ordinary electric steel is assumed to be 750 kWh per ton as this is a normal

TABLE IV.—EFFECTS OF TYPE AND QUANTITY OF SPONGE IRON IN ELECTRIC FURNACE MELTING

	Degree of red.	Analysis			Kgs. of sponge per ton using		Slag kg./ton of sponge	Charcoal kg./ton of sponge	Extra power kWh/ton of sponge
		Fetot	Os	G	100% Sponge	70% Sponge			
Type of Sponge Iron									
Söderfors from 71·5% concentrate ..	93	95·50	1·92	2·58	1096	767	28·8	20·3	79·3
" " 65·0% "	90	83·57	2·39	14·04	1265	886	154·9	21·3	163·8
" " Striberg, hot conc. ..	90·3	56·50	1·58	41·92	1953	1367	461·5	8·3	304·1
" " " conc.	89·96	87·13	2·51	10·36	1209	846	115·6	23·2	145·7
Höganäs fr. 71·5% concentrate	96·0	97·27	1·11	1·62	1075	753	18·1	14·1	46·9
Unreduced Concentrate									
71·5% Fe	—33·3	71·50	27·31	1·19	1460	1022	17·6	222·8	915·5
65·0% Fe	—33·3	65·09	24·85	10·15	1622	1136	116·0	200·9	886·8
Pellets fr. conc. with 71·5% Fe	—50·0	69·14	29·71	1·15	1510	1057	17·4	242·2	990·0
Concentrate required for this	—	—	—	—	1540	1078	—	—	—

figure for a 10-ton electric furnace. Consumption of graphite electrodes, a normal figure being 5 kg. per ton of steel, is increased in direct proportion to total power consumption. The remaining costs are for ordinary electric steel 60s. 8d. per ton. Half of these are assumed to be constant per ton of steel produced, the other half directly proportional to the time consumed. This time in its turn is set directly proportional to power consumption per ton of steel. Power consumption per ton of steel is calculated from the figures for power consumption per ton of sponge iron from Table IV and multiplied with the sponge iron consumption at 70% sponge iron, which figures are also given in Table IV, 750 kWh are then added to these figures.

As the sponge iron plant is supposed to be located close to the mine a freight of 6s. 11d. from mine to steel plant is added to the cost of sponge iron.

It can be seen from Table V that the production cost of ingot is at its lowest point when Höganäs sponge iron from concentrate with 71·5% Fe is used as raw material. The costs for steel from Wiberg sponge iron from normal sinter is, however, only slightly higher. Figures for steel made of Wiberg sponge iron from pellets are not given as the assumption that the pelletizing is only half as costly as normal sintering is rather uncertain. If it holds true, however, the ingot cost can be lowered to 303s. 7d. per ton.

Quite a few experiments with melting of various types of sponge iron in electric furnaces have been carried out in the United States, mostly by the Bureau of Mines.[17, 18, 19, 20] The sponge iron behaved quite normally in the furnace and corrosion of the linings was not evident. The bulkiness of the charge seems to have been of some disadvantage. In the more successful heats power consumption was 800 kWh per ton of steel, while iron yield was 90 to 95%.

B. Acid open-hearth furnace.—The most interesting undertaking in Sweden regarding the use of sponge iron has been to investigate the possibilities of increasing the use of sponge iron in the acid open hearth. The above-mentioned committee has devoted most of its efforts to this problem. This work was divided into two main lines: the melting of sponge iron briquettes where carbon, silicon and manganese were added to these briquettes to form a synthetic pig iron; and melting of ordinary sponge iron, adding carbon, silicon and manganese in the furnace. The first of these methods was proposed by Wiberg as long ago as 1927, but real experiments have never before been carried out. After some preliminary tests the following composition of the briquettes was decided upon:

Charcoal	1%
Graphite	3%
Si	0·5%
Mn	0·5%
Höganäs sponge iron ..	balance

Full scale experiments were performed in the acid open hearth at Hellefors with 30, 50 and 65% of this sponge iron in the charge. The scrap amounted to 35%, in all cases the rest being pig iron. The trials did not succeed too well apparently because of too low carbon content as well as silicon and manganese. Carbon content at the melt was lower than normal and the silicon pickup was more difficult than normal.

The other experiments were carried out at Hofors at the initiative of *Bohm*. Here normal Höganäs sponge iron cakes were charged together with a constant amount of 30% domestic scrap and the sponge iron replacing

TABLE V.—PRODUCTION COST OF ELECTRIC STEEL.

	Normal electric steel.		Electric steel with 70% of Wiberg sponge iron.				Electric steel with 70% of Höganäs sponge iron	
Raw material for sponge			Sinter (Conc. 71·5%)		Sinter (Conc. 65%)		Concentrate 71·5%	
Fe-content in sponge %			95·50		83·57		97·27	
Degree of reduction %			93		90		96	
	amount	sh.	amount	sh.	amount	sh.	amount	sh.
Charcoal pig iron, 276/– per ton	215	59/4	—	—	—	—	—	—
Domestic scrap, 207/– per ton	323	66/11	323	66/11	323	66/11	323	66/11
Purchased, 1 : a scrap, 276/– per ton	537	148/3	—	—	—	—	—	—
Sponge Iron, 174/3 per ton	—	—	767	133/7	—	—	—	—
Sponge Iron, 143/– per ton	—	—	—	—	886	126/8	—	—
Sponge Iron, 177/6 per ton	—	—	—	—	—	—	753	133/7
Freight, sponge iron, 6/11 per ton	—	—	—	5/3	—	6/1	—	5/2
Additions + lime + fluorspar	—	18/9	—	18/9	—	18/9	—	18/9
Charcoal briquettes, 345/– per ton	—	—	15·6	5/5	18·9	6/6	10·6	3/8
Power, 27/7 per 1,000 kwh.	750	20/8	811	22/5	895	24/8	785	21/8
Electrodes, 2/2 per kg.	5	11/–	5·41	11/11	5·97	13/2	5·33	11/7
Remaining costs (constant/ton)	—	30/4	—	30/4	—	30/4	—	30/4
Remaining costs (constant/hour)	—	30/4	—	32/10	—	36/3	—	31/9
Total shillings	—	385/7	—	327/5	—	329/4	—	327/5
Be deducted: scrap, 207/– per ton	40	8/3	40	8/3	40	8/3	40	8/3
Total shillings/ton ingot	—	377/4	—	319/2	—	321/1	—	315/2

pig iron in various percentages. To the charge were also added carbon as charcoal, graphite turnings or briquettes of charcoal and ferrosilicon and silicon-manganese.

The following practice was finally used: Pig iron, if any, was charged together with FeSi (26% Si) and FeSiMn (20% Si, 50% Mn) on the slopes. Following this came the charcoal briquettes equally spread out over the whole furnace and after them all the scrap, which was charged as near the slopes as possible. Finally all the sponge iron was charged.

Some 100 heats were made with sponge iron in the charge varying from 0–70%. All heats were quite normal in all respects. In Table VI, data from one of the heats can be seen compared with data from a normal heat.

TABLE VI.—DATA FROM 2 OPEN HEARTH HEATS AT HOFORS.

		F-2035	F-2036
Steel, quality, killed, C-content	%	0·35	0·35
Charge: Charcoal pig iron	%	51	—
Rolling mill scrap	%	49	30
Normal uncompressed sponge	%	—	70
Total	%	100	100
Total charge	kg.	23,300	23,000
Briquettes of charcoal	kg.	—	1,360
26% FeSi	kg.	—	675
20/50% FeSiMn	kg.	—	160
Carbon content of the charge, calculated:			
Excl. carburizer	%	2·65	0·15
Incl. carburizer	%	—	5·17
Contents of Si and Mn in the charge, incl. FeSi and FeSiMn, calculated:			
Si	%	0·4	0·97
Mn	%	0·75	0·47
C-content at melt	%	—	1·82
C-content at 1st ore addition	%	1·75	1·70
Feed ore	kg.	675	575
Times: Melting	hours	6·00	7·25
Refining	"	4·33	3·15
Preparation of the furnace (normal)	"	1·30	1·30
Total time	"	11·63	11·70
Actual preparation time	"	1·70	1·60
Obtained ingot + ingot ends	kg.	22,105	22,995
Ingot recovery of charge excl. ore additions	%	94·8	100·0
Ton ingot per total hour		1·90	1·96

The following conclusions can be drawn: Production rate was normal and sometimes higher than normal. Unbriquetted sponge iron is to be preferred to briquetted. The silicon may just as well be added in the furnace as briquetted into the sponge iron. Efficiency of carbon added was as follows:

	%
Graphite turnings	35–45
Briquettes of charcoal	30
Charcoal breeze	0–10

Many experiments of this type have also been made at Långshyttan, but there the experience has been that the furnace bottoms were corroded with higher percentages of sponge iron. It may, therefore, be true that sponge iron addings in the acid open hearth will be limited to 35–50%.

Regarding the charging of extra additions the following practice seems to be correct (in percentages of sponge iron and with 70% sponge iron in the charge).

8·5% briquettes of charcoal
3% 26%–FeSi
1·5% FeSiMn 20/50

Some experiments with lower iron content in the sponge (90·3%) showed a decrease in iron yield from 96–97·5% to 90% and an increase in slag weight from 9–18% of ingot weight.

It is generally believed that it is a great advantage to have as high an iron content and degree of reduction as possible in the sponge iron. The following calculations are, therefore, based on this grade. It may, however, be pointed out that the lower degree of reduction of Wiberg sponge iron (93% for a concentrate with 71·5% Fe) is somewhat compensated for by the carbon content (0·7%). Some apprehensions, that the tendency of the Wiberg sponge iron to produce fines might be a disadvantage in the acid open hearth, have not proved valid and thus it is not necessary to briquett this type of sponge iron either.

Table VII shows production cost for various percentages of sponge iron in the charge. The pig iron is in all cases assumed to be added as cold metal. The savings according to the use of sponge iron amounts to 20s. 8d. to 34s. 6d. per ton of ingot for the assumed costs. If hot metal is used the normal production cost is lowered to 394s. 8d. compared with 409s. 2d. for cold metal. The use of hot metal is especially favourable when moderate additions of sponge iron are made because of slower oxidation of carbon, silicon and magnanese than for cold metal. It should be pointed out that the use of sponge iron in larger amounts in acid open hearth has only been tried experimentally. The technique of using sponge iron certainly will be improved if sponge iron is available at low cost.

C. Acid high-frequency furnaces.—The normal charge in these furnaces is cold and consists of pig iron, domestic circulating scrap and remelting material from basic open hearth. Due to shortage of this last material during recent years it has been replaced increasingly by Höganäs sponge iron.

The best melting results have been made with the normal uncompressed type of sponge iron. Bofors has used this sponge iron in greater and greater amounts making about 1,000 heats during the first four months of 1947 with 40% Höganäs sponge iron in the charge. The following general conclusions can be drawn:

A sponge iron percentage above 40% tends to decrease production per hour and increases iron loss and power consumption. Iron loss is about 4–5% for 1·5 ton conical and 2–3% for 4·5 ton cylindrical furnaces.

TABLE VII.—PRODUCTION COST OF ACID OPEN-HEARTH STEEL WITH VARIOUS PERCENTAGES OF HÖGANÄS SPONGE IRON

Sponge Iron in the charge	0		20%		35%		50%		70%	
	kg.	sh	kg.	sh.	kg.	sh.	kg.	sh	kg.	sh.
Cold metal, 276s. per ton	765	211/2	546	150/8	379	104/7	218	60/2	—	—
Domestic scrap, 207s. per ton	328	67/11	328	67/11	328	67/11	328	67/11	328	67/11
Sponge iron, 184s. 5d. per ton including freight 6s. 11d. per ton	—	—	210	38/9	372	68/7	528	97/4	739	136/3
Additions (C, Si, Mn)	—	—	—	—	—	12/6	—	24/2	—	40/–
Feed ore and normal additions	—	17/10	—	17/10	—	17/10	—	17/10	—	17/10
Remaining costs	—	120/6	—	120/6	—	120/6	—	120/6	—	120/6
Total	—	417/5	—	395/8	—	391/11	—	387/11	—	382/6
Be deducted: scrap 207s. per ton	40	8/3	40	8/3	40	8/3	40	8/3	40	8/3
Total shillings per ton of ingot	—	409/2	—	387/5	—	383/8	—	379/8		374/3

TABLE VIII.—THE VALUE OF SPONGE IRON IN COMPARISON WITH CHARCOAL PIG IRON WHEN MAKING ELECTRIC STEEL WITH 70% SPONGE IRON IN THE CHARGE
(Pig iron 276s. per ton)

	Calculated cost of production of sponge iron including freight sh./ton	Required amount of sponge iron kg./ton of steel	Cost of ingot sh./ton	Value of sponge	
				sh./ton	% of sponge iron
Normal electric steel	—	—	377/4	—	—
Type of sponge iron					
Wiberg sponge iron :					
From conc. 71·5% Fe	181/2	767	319/2	257/7	93·3
„ „ 65 % Fe	149/10	886	321/1	213/8	77·4
Höganäs sponge iron :					
From conc. 71·5% Fe	184/5	753	315/2	267/3	96·8

The sponge iron should be added last and the charging should be rapid in order to avoid corrosion of the crucible by the steel and the slag formed. As soon as the charge is melted the slag should be removed and replaced by a more neutral one, for example blast-furnace slag. The lime content of this is beneficial. As the sponge iron is melted under oxidizing conditions it is advisable to clear the bath with a short silicon pickup.

The use of sponge iron in acid high-frequency furnaces is rather new and more experience must be gained. The possibility of using other carbonaceous materials instead of pig iron should be investigated.

Calculations of the Value of Sponge Iron in Comparison to Pig Iron

The calculations presented for production cost of various types of steel on the basis of sponge iron make it possible to calculate the value of sponge iron as compared to pig iron. The cost used for charcoal pig iron, 276s. per ton refers to the present situation and is possible to obtain only in a modern blast furnace with high production and through the use of rich sinter. It should be emphasised that the relationship between sponge iron and pig iron is more favourable at higher pig iron costs.

The results of the comparisons are shown in Table VIII referring to electric steel. The value of the richer sponge iron is, of course, higher than that of a sponge iron with a lower iron content, but the production cost of the former is usually higher.

For acid open hearth the comparisons (Table IX) have been carried out only for Höganäs sponge iron from a 71·5% Fe concentrate. The comparison is here complicated because of the fact that the value of sponge iron is dependent upon the percentage of sponge iron in the charge. At, for example, 20% the value of sponge iron is 104% of that of pig iron, while at 70% it is only 84%. Too few experiments have been made to correctly fix the relationship between the value of iron sponge and hot metal.

When competing even with the cheapest possible charcoal pig iron it can be seen from the above calculations that using sponge iron in the electric and acid open-hearth furnace yields a considerable profit. The same is true when sponge iron is used in high-frequency furnaces. In this last case it seems as if the value of sponge iron should be much higher than that of pig iron because it replaces a material made by melting pig iron.

Effects of Sponge Iron on Steel Quality

The excellent quality of steel made from sponge iron has been confirmed at the Söderfors works where electric steel has been produced almost entirely from sponge iron. As mentioned before Höganäs sponge iron has been regularly used in the acid open-hearth process for many years and is generally believed to have improved the quality considerably.

One obvious advantage of the use of sponge iron is the regularity of the melting operation and of the steel analysis. Thanks to the low temperature used in producing sponge iron no elements, apart from small quantities of carbon, are added to the iron, which means that the composition of sponge iron varies much less than that of pig iron. Thus when sponge iron and domestic scrap are used, and the complete composition of the charge is known, it is possible to carry through the melting and refining with great accuracy, and it is clearly of great advantage to a steel maker to know that variations in steel quality cannot, at any rate, be due to variations in raw material.

The purity of sponge iron is also of great importance to-day in avoiding contamination, particularly in view of the tendency for Cu, Sn, Ni and Cr to increase considerably on account of the difficulty in obtaining clean scrap of known analysis.

Considerable discussion has taken place on the importance of the use of virgin raw materials in steel production, and if this qualification can be applied to any material, it can certainly be applied to sponge iron, which is never melted. The advantage of material low in hydrogen and nitrogen is obvious, and sponge iron is free from both these elements, whereas other low carbon materials, such as Bessemer are not free from nitrogen.

In Söderfors the carbon contents of the Wiberg sponge vary from 0·5–1%, whilst Höganäs sponge iron normally contains less than 0·1%, so that very low carbon contents can be obtained when melting sponge iron. Melts using Höganäs sponge exclusively have shown carbon contents of 0·003–0·004% C, figures which will interest producers of low carbon stainless steel, deep drawing steel and steel for transformer sheets, etc.

Considerations Affecting the Method of Sponge-Iron Production and the Raw Material for Sponge Iron

All the above calculations have been made in order to analyse clearly the rather complex problem the Swedish

TABLE IX.—VALUE OF SPONGE IRON IN THE ACID OPEN HEARTH IN COMPARISON WITH COLD METAL (CHARCOAL PIG IRON)
(Charcoal pig iron 276s. per ton, Höganäs sponge iron 184s. 5d. per ton)

Sponge iron in charge %	0	20	35	50	70
Cold metal	70	50	35	20	0
Cost of ingot, sh./ton	409/2	387/5	383/8	379/8	374/3
Sponge iron value, sh./ton	—	284/6	252/11	240/2	231/4
„ „ „ % of cold metal cost	—	103/9	91·6	87·0	83·8

quality steel producers have to face having two satisfactory sponge iron processes at their disposal. As has been said before it is no easy task to advise in this choice of sponge-iron production particularly since no detailed production cost is available for the Höganäs process, and it is not known under what conditions it can be acquired. Some help in answering this question would, however, be given by summarizing the advantages and disadvantages of the two processes.

The Höganäs method can be said to have the following advantages :

1. The raw material can be any crushed ore with a grain size less than ½ in. There are no limits as to minimum size of the concentrate.
2. Generally no sintering or other treatment of the concentrate other than drying is needed. The process accomplishes a certain desulphurisation of the raw material. Experiments with various concentrates with sulphur contents varying from 0·020 to 1·40% S show a desulphurisation on an average of 63%.
3. The Höganäs process makes it possible to obtain a high degree of reduction, about 96%. If the iron is also present in the silicates the reduction is, of course, lowered, which is true for any sponge iron process.
4. The cheapest possible fuel can be used for reduction and heating. The greater part of the reduction material is now coke breeze, while the heating gas is generated from very low grade coal. The total fuel consumption is remarkably low being about 430 kg. pure carbon per ton of sponge iron.[9]
5. The finished product is obtained as cakes rather porous (density 2·0 kg./dm.^{3}), it is true, but notably strong and free from any tendency to form fines.

Disadvantages of this method are :

1. Construction costs high.
2. Labour costs rather high.
3. Lump ores and some ores with high sulphur content cannot be reduced by this method. The lowest sulphur content, which can be obtained is about 0·010%.

The clay containers were formerly the weakest part of the process, but this problem is said to be capable of solution by improved material in the containers and other changes of construction. The process as a whole is under intensive development which may lead to quite a new type of furnace making it possible to decrease labour cost as well as fuel and maintenance.

The *Wiberg* process has the following advantages :

1. Sinter as well as lump ores can be reduced. If the sulphur content of the ore is high it can be reduced to very low figures by sintering and also by the oxidizing heating in the upper parts of the furnace shaft.
2. The Wiberg process can use Swedish fuel as a reduction agent, which fact can be of value if Sweden is isolated.
3. The furnace is relatively cheap in construction.
4. The process is continuous and well mechanized and labour cost accordingly is low.
5. As a great part of the heat needed is supplied by water power the process can utilise peak spring-time power and other secondary energy.

Disadvantages are :

1. The concentrated ores have to be sintered before reduction which makes the process more expensive.
2. Inferior fuel or fuel in form of breeze cannot be used.
3. It is difficult to obtain a high degree of reduction. Using rich sinter it is possible to reach 93%, while sinters with lower iron content show 90% or less.

It is true for both the Höganäs and Wiberg processes that improvements can be made leading to lowering of production cost. As regards the Höganäs process the efforts ought to be directed towards a greater mechanization in order to decrease labour costs. Regarding the Wiberg method the pelletizing process may make it possible to lower production cost.

Sweden has certainly great resources of ores suitable for production of sponge iron. As previously mentioned many different types can be used. Some limitations may, however, be pointed out. The content of iron tied up in silicates, which cannot be reduced without melting, ought to be as low as possible. The same is true for phosphorus if the sponge iron is going to be used for making quality steel.

As a raw material for the Höganäs process iron ores with low contents of sulphur and phosphorus are likely to be preferred even in the future. It is a very promising fact that it is now possible to make concentrates with up to 71·5% Fe even from ores located in the middle of Sweden.

Experiments on an industrial scale carried out at Grängesberg with a new extraction method for the removal of phosphorus have been successful. Hereby low phosphorus concentrates can be made available for the quality steel industry in much larger quantities than was thought possible before the development of this method. Other experiments with quartzose hematites give promise of a successful process for roasting to magnetite state followed by a magnetic separation of these ores, whereby they certainly can be used more economically than was possible before.

Throughout this study it has been assumed that sponge iron can only be a substitute for charcoal pig iron or material specially produced for remelting. All calculations of cost have been based on present costs.

The supply of charcoal in the future is likely to be more and more restricted and its cost per calorie increased, due to competition of the pulp industry for the available raw material, as well as the increasing labour costs of charcoal production.

If sponge iron were freely available there would be a demand for it in Sweden to-day of about 130,000 tons per year distributed among the various types of furnaces with 70,000 tons in acid open hearth, 50,000 tons in arc furnaces and the rest in high-frequency furnaces and basic open hearth. To-day's production of sponge iron is about 30,000 tons per year. Therefore, the consumption of charcoal pig iron could be decreased by 100,000 tons per year, if sponge iron were introduced on a larger scale. The greatest gain from this would, of course, be that the consumption of charcoal could be decreased by a third of its figure to-day and that this charcoal could be replaced by imported fuel such as coke breeze or low-grade coal. In Table X some figures are given for consumption of fuel, power and labour when producing 100,000 tons of charcoal pig iron or sponge iron respectively.

The installed capacity, equivalent to 85 mill. kWh per year for the Wiberg process, is 12,000 kW. The two

TABLE X.—COMPARISON OF MATERIALS, ETC. REQUIRED FOR SPONGE AND PIG IRON PRODUCTION

	Production ton/year	Charcoal cu.m/year	Coke ton/year	Coke breeze ton/year	Coal ton/year	Power kWh/year	Labour men
Charcoal pig iron	100000	450000	—	6000	—	—	200(130)
Sponge iron : Wiberg	100000	—	20000	7000	—	85 mill.	100
Sponge iron : Höganäs	100000	—	—	55000	12000	—	150

figures for labour, when making charcoal pig iron, correspond to old and modern types of blast furnaces. It should be pointed out too that a third of all labour, used for making charcoal could be released for other purposes when converting to sponge iron. According to a recent investigation this would mean that about 1,500 men could be used for other purposes.

Some may wonder why the Swedish steel industry has not changed over earlier to sponge iron. The answer is, neither of our sponge-iron methods has been fully developed until recently. Besides that, the Höganäs process has not previously been available for the steel industry. Nor could it be realised before that the fuel situation would be as complicated as it is to-day.

The most difficult thing, however, is to form an opinion about the future of this problem. It is generally believed that the reason that Swedish steel has been able to hold its place in the world market is that it is based on charcoal pig iron as a raw material. The only suitable substitute for charcoal pig iron is high-grade sponge iron. Perhaps some people would say that Sweden could just as well adopt the practice followed in other countries where high-grade coke pig iron or good scrap is the base raw material. We think that would be a dangerous step. The production of sponge iron is a more natural way for Sweden to use pure ores and it is sounder to produce the material directly for melting, thus avoiding contamination with coke and the necessity for a subsequent refining period with the attendant possibility of overheating.

It may be possible that the production of high-quality steel in Sweden will follow two lines in the future : one based on refinement of coke pig iron and scrap and the other based on charcoal pig iron or sponge iron. Due to this the need for the latter may be smaller than can be estimated to-day, but it should always be important to maintain the possibility of producing steel of the highest possible quality.

It is certainly a great advantage to have the choice to-day of two sponge-iron processes particularly as they supplement each other in important aspects. Various ores can be used as well as various types of fuel.

Which process is chosen is more or less a question of what can be estimated regarding the cost of fuel and power in the future. As far as can be determined we must count on an increase in the cost of electric power. The cost of imported fuel, on the other hand, should go down. A certain shortage of coal suitable for the production of blast-furnace coke is felt all over the world. It seems certain that the cost of high-grade coke will be very much above the cost of coke or anthracite breeze suitable for the Höganäs process. Against this can be weighed the advantage of the Wiberg method in requiring less labour.

As stimulating competition has always proved to be a motive for progress, it is hoped that a new and modernized Höganäs plant will be erected probably based on high-grade concentrates from Grängesberg. This would mean a much needed addition to the raw material supply for our quality steel industry, a decrease in the need of charcoal and a lowering the production cost of steel.

The main author wishes to thank his co-workers in the sponge-iron committee and the steelworks : Sandviken, Hofors, Långshyttan, Hellefors, Bofors, Söderfors and Höganäs for their willingness to make experiments. It is because of this combined effort that it has been possible to get the quick results on which this analysis of the sponge-iron problem has been based.

Contributions to the Discussion on the Subject in Sweden

When Dr. Tigerschiöld presented his paper at the May meeting of Jernkontoret, 1947, ten prominent Swedish metallurgists gave valuable contributions to the lively discussion.

Mr. E. Ameen who previously was director at Söderfors stressed the point that in Sweden sponge iron probably could compete with coke pig iron when rich ores are used. According to his calculations sponge iron and coke pig iron could be manufactured at the same cost when coke and electric power were available at the following prices :

Coke sh/ton		Power, sh/1,000 kWh
s. d.		s. d.
27/7	....	11/–
41/5	....	16/7
55/2	....	22/1
69/–	....	27/6
138/–	....	55/–

However, as Dr. Tigerschiöld had pointed out, the value of 1 ton of sponge iron in comparison with coke pig iron varied according to the steel-making process used. Mr. Améen also mentioned the fact that the coke ash contains many foreign elements which have influence on the quality of the steel. Among other elements as much as 1% of germanium and arsenic have been found in coke ash.

Professor M. Wiberg pointed out that a more thorough investigation should be made with reduction of rich lump ores from Kiruna and other mines in Norrland. In this part of Sweden water power is very cheap. When using lump ores there is no need for roasting or sintering of the ores whereby the investment cost as well as the cost of production will be lowered. He also mentioned that earlier experiments had shown that a rate of reduction of 95% had been obtained by reducing a rich sintered ore in a small experimental furnace at Domnarvet, and he thought that a suitable construction of the furnace could improve the rate of reduction.

Professor B. Kalling was not as pessimistic as Mr. Améen regarding the detrimental influence of small amounts of foreign elements in the coke ash, and pointed

out that many ores and above all ferro alloys contain high amounts of the same elements.

Mr. E. Sunström had made heats in an electric arc furnace at Bofors using 30% and 70% respectively of sponge iron in the charge. In some cases the sponge iron used had been manufactured in Höganäs and in other heats a Wiberg sponge with lower iron content was charged. The report which was very complete, confirmed the calculations made by Dr. Tigerschiöld.

Mr. I. Bohm had made heats in the acid open-hearth furnaces at Hofors and of special interest were the trials where pig iron was charged as hot metal. By using 35% hot metal, 35% sponge iron and 30% domestic scrap the addition of charcoal briquettes for carburizing could be decreased by about 50% in comparison with heats made with the same amount of cold pig iron. The value of sponge iron was therefore higher than previously calculated.

Mr. G. Helmer had made experiments in an arc furnace at Sandviken and found that by using various percentages of Höganäs very rich sponge iron no increase in the consumption of power against ordinary charges occurred. By using Söderfors sponge the extra power was 20–25% lower than could be calculated from the equations given by Dr. Tigerschiöld.

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Allocations of Tin Metal

The Ministry of Supply announces the interim allocations of tin metal made by the Combined Tin Committee for the first half of 1948, amounting to 17,703 long tons. The allocations now made represent more than half of the total allocation that each country can expect for the first six months of this year, in view of the estimated production of tin metal available for export up to June 30, 1948, and after taking into account the probable requirements of many countries which have not yet been presented to the Committee. When this information has been supplied, allocations will be made to such countries on the basis of the same standards used in computing the allocations listed below.

The Committee regrets that the supplies of tin metal available for allocation during the first six months of 1948 will fall short of the amount available during the last half of 1947, mainly because all the war-time stock-accumulations found in the Far East have now been distributed.

A revised questionnaire calling for final date for second half 1947 is being forwarded very shortly to representatives of consuming countries. Replies are expected by March 1st to enable the Committee to make final allocations for the first half of 1948 later in that month.

The first interim allocations for 1948 are as follows:

Country	Amount (long tons)	Country	Amount (long tons)
Canada	1,090	India	1,400
China	32	New Zealand	146
Czechoslovakia	336	Palestine	55
Denmark	160	Poland	520
Finland	60	Switzerland	200
France	2,720	Turkey	140
Germany U.S./U.K. Zone	324	United States	10,200
Germany French Zone	120	Others	100
Hong Kong	100		
		Total	17,703

Supplies may be obtained from the following sources: The United Kingdom, on behalf of the United Kingdom and Malaya; Hong Kong; the Netherlands; Belgium; China and Siam. In addition, small demands of certain Latin American and Middle Eastern countries may be met from the above sources and the United States.

Further information as regards procurement may be obtained from the Secretaries of the Combined Tin Committee or from the Directorate of Non-Ferrous Metals, 20, Albert Street, Rugby.

Hiduminium Technical Data

Those familiar with previous issues of Hiduminium technical data will appreciate the practical way in which these are presented for convenient use of designers and engineers who are increasingly applying aluminium alloys for many purposes. The recent issue is presented on somewhat similar lines, but changes will be noted in the numeration of the alloys. They are now given a numerical grouping which is distinctive and also has a functional significance. The alloys are in three groups: In group A the digit indicating a grade is repeated to show that wrought alloys are referred to; in group B a cypher follows a digit, indicating a cast alloy; while in group C a digit followed by a dissimilar digit indicates engine alloys and those suitable for elevated temperatures.

As with other materials the choice of a particular aluminium alloy depends on the application in view, but this useful data book of 60 pages gives comprehensive information on composition, physical and mechanical properties of the standard wrought and cast alloys in the "Hiduminium" range, and it is invaluable for reference purposes. It is published by High Duty Alloys, Ltd., Slough, Bucks., copies of which are available on request.

Metallurgy and Atomic Energy

By C. Hubert Plant, F.I.M.

Various aspects of the subject from a metallurgical point of view have already been discussed by the author in this short series of articles. In the present article, the third of the series, the author shows that the most advantageous elements for use as liberators of energy are those that occupy either end of the periodic table. Those of low atomic masses and charges give energy of surface tension, while those of high atomic mass, with high positive charges produce energy by liberation of those charges.

DURING school or college days and when endeavouring to obtain some knowledge of physics or chemistry, two matters have caused considerable trouble to many. The first was the so-called law of the conservation of matter. We read or were told that in 1774, the great French chemist, Lavoisier had stated that " Nothing can be created, and in every process there is just as much substance present before and after the process has taken place. There is only a change in the form of matter." Now all chemical experiments appeared to verify this statement and it was, until the advent of Einstein, considered to be an inviolable Law. Following Planck's Quantum Theory to which reference has already been made we also referred to the fact that Einstein was able to prove that energy had equivalent mass in accordance with the equation :

$$e = mc^2 \quad .. \quad .. \quad .. \quad 1$$

where e is energy, m equals mass and c is the velocity of light. Furthermore, when there is any emission of radiation of whatever kind, it was shown that there is loss of mass equal to :

$$m = \frac{e}{c^2} \quad .. \quad .. \quad .. \quad 2$$

which relation is, of course, derived from the statement of equation 1.

Now in a great many chemical reactions there is liberation of radiation in heat or in some other form, so that if the above is correct, mass is lost and the law of conservation of matter cannot be correct. This was not easy to prove from the chemical standpoint, but when atomic energy is considered the point becomes very clear. For instance, the alpha particle consists of two protons and two neutrons and it is simple to show that, if it be assumed that these four particles are moving about individually as two positively charged particles and two neutral particles and, due to some reason, they coalesce together to form the helium nucleus, there will be a loss of mass in the aggregate of nearly 0·7%. This result can be arrived at as follows :—If the mass of the proton and the neutron be reckoned as 1·0078, then two protons and two neutrons will produce a combined mass of 4·0312. But the atomic weight or mass number of helium is 4·003 which gives a difference of 0·028. Now consider what happens when two protons come together to form heavy hydrogen. It might be expected that the mass of the nucleus of heavy hydrogen would be just twice the mass of the hydrogen proton, but instead its mass is 2·0136 showing a loss in mass of 0·002 units. Under these circumstances it certainly appears that twice one is not always two, also that mass has disappeared. At first sight it would appear that the differences mentioned are so small as to be entirely negligible, but this is not the case, for if these small differences are computed in energy and expressed in electron volts, it means the equivalent of something of the order of 1,000,000 volts. In the case of hydrogen of mass 3, or tritium, the release of energy will obviously be greater and this point should be borne in mind in connection with later arguments.

The suggestion has just been made that two protons and two neutrons should coalesce to form a helium nucleus and that they do so is obvious since helium gas is a fairly ordinary element, also two protons existing together as heavy hydrogen is now a well-known phenomenon. But the question at once arises—how does this come about ? It is an elementary rule in electricity that like particles repel and unlike ones attract. How then, do positively charged particles in any nucleus live together in apparent serenity when, by all the laws, they should be repelling each other with the probable break up of the nucleus.

The answer to this riddle was first explained by G. Gamow in America and later developed by Neils Bohr and J. A. Wheeler with some very illuminating results. The general argument is somewhat intricate and is beyond the scope of these articles, but the conclusions can be described. The first essential of the theory is to consider the nucleus to be exactly akin to a single drop of ordinary fluid, and as is well known fluids are subject to powerful forces known as surface tension and cohesive forces. Since the mass of the proton and neutron is always the same, if a nucleus be looked upon as " nuclear fluid," its density must also always remain the same, no matter what its size may be. Gamow was able to calculate the density of this nuclear fluid and obtained the astonishing result which translated into ordinary figures means that a cubic inch would weigh about 3,720,000,000 tons, assuming that it was concentrated to form continuous matter. The surface tension is also, therefore, colossal, and the energy required to remove one particle from the surface of a nucleus is of the order of 5,000,000 electron volts.

To develop the idea further, if two of these drops of nuclear fluid come together the total surface of the double drop will be less than that of the two single drops. This is a simple sum in spherical geometry, the reduction in surface varying with the relative sizes of the two drops if both are not the same diameter. As there is less surface, the fusion of two such droplets must lead to the liberation of surface energy and in view of the fact that it is the tendency of nature for fluids to

always occupy the least space the natural result would be for all nuclei to ultimately fuse together into one agglomeration of the intensely dense matter just described. It is here that the repelling force of the positively charged protons comes in to prevent a calamity because these repulsive forces are acting in the opposite direction from the forces of surface tension, and while the latter is inclined to bring together into one whole, two or more droplets which are close together or to weld any one drop more solidly, the former are exerting repelling energy tending to force the drop asunder or to keep apart those which are close together. The force which is the stronger is the one which obviously wins the battle. Another very important point which must be borne in mind is that the charge energy of two identical drops is less than that of one drop formed from the two, which is the opposite from the action of surface tension. The important conclusion emerges, therefore, that in coming together, two drops increase their surface tension with liberation of energy, but reduce the total electric energy, with conservation of this force.

So far, consideration has only been given to the two lightest elements of the periodic table, hydrogen and helium, but it is necessary to discover what happens at the other end of the scale in connection with the heavy elements such as uranium and thorium. Now there is a mathematical ratio between the total surface of the nucleus and the atomic weight of each element which equally affects the surface energy compared with the atomic weight. The relation is that the surface energy is proportional to the square of the cube root of the atomic weight, or put more simply, it is proportional to two-thirds power of the atomic weight. But against this, the nuclear charge is approximately proportional to the atomic weight or mass number and as the electric energy increases as the five-thirds ($\frac{5}{3}$) power of the charge, that is about the square, it will be seen that the electric energy increases at a much faster rate than does the surface tension energy. This means that with the heavy elements the first tendency is for the nucleus to break apart due to the excessive electric energy, while the energy of surface tension is in this instance acting as a brake on the repelling forces of the similar charges on the protons. It will now become more clear why it is that all the radioactive elements are those containing the greatest mass, resulting in the spontaneous disruption of the nuclei.

But yet another point arises. If the energy of surface tension is gradually decreasing along the atomic scale in the upwards direction and the electric energy is gradually decreasing along the atomic scale in the downwards direction, there must be a point somewhere in the periodic table where neither the one nor the other is likely to be the greater and the nucleus must be entirely stable. That is, the surface tension energy must balance the electric energy. Bohr and Wheeler have proved this to be the case, and the element which possesses this degree of stability is the element silver of atomic mass 108 and atomic number 47, or to be more exact, it is the centre element of the stable range, as differences are so slight on either side. There is, therefore, a tendency for all elements below this in the atomic table to fuse together releasing surface energy, while those above it in the atomic table ought to break up with liberation of internal electrical energy. If this were to be so, it would have happened long ago, and the only element of which we should have any cognisance would be silver.

The problem to be solved now is—why has not this happened and how is it that with the exception of radioactive elements, all other elements appear to exist easily in the stage in which they have always been known since chemistry and metallurgy were studied. For an explanation of this point, the science of chemistry will give a very good answer. Consider two very simple reactions. First consider the electrolysis of water and secondly, the preparation of hydrogen by the schoolday experiment of adding hydrochloric acid to zinc. In the first instance there is a very stable compound water, and in the second instance an element, zinc and a compound, hydrochloric acid, both of which show no tendency to instability. But, if an electric current is passed through the water, it is disassociated into the two gases hydrogen and oxygen, while if the acid is poured onto the zinc, a chemical action takes place, liberating hydrogen and leaving behind zinc chloride. Now the point of all this is, that these three substances, water, zinc and hydrochloric acid are perfectly content to remain as they are unless something is done to them. In the one case electric energy is introduced and in the other case the two substances are merely brought into close proximity to each other. But in both cases there is immediately a re-arrangement of atoms with the well known results, and this re-arrangement takes place-comparatively quietly and easily. But now consider another experiment of our schooldays. Soak some cotton wool with nitric acid, leave it loose and dry it, then pack it tightly together and introduce a match to it. There will be quite a violent explosion as many budding chemists have found to their cost. And lastly consider trinitro-toluene or TNT as it is generally referred to and imagine striking a cake of this material with a hammer. The difficulty here is that the experimenter would never know the results of his action. In both the instances just cited, there is again a re-arrangement of atoms, but contrary to those mentioned above, the action is so excessively rapid and so much energy is liberated so quickly that it is termed an explosion. Another point should be noted and that is that in the so-called chemical reactions such as the zinc-hydrochloric acid one, the two substances are introduced to each other to produce the re-arrangement of atoms, but in explosions there is the re-arrangement in the interior of the substance itself. The atoms are all present and not in a very comfortable position, as it were, so that the application of heat or strong vibration gives them the chance of moving to more comfortable quarters and they do so with extreme speed and apparent violence.

This produces the conclusion that although the substances to which reference has been made are to all intents and purposes normally stable, actually they are not so, but are what is termed metastable, requiring some outside urge before they can take up different properties. In the actions relating to atoms, this outside urge is termed the activation energy and is the energy required to cause something to happen.

Reverting now to the subject of nuclear reactions, it will no doubt have been realised that the atoms which tend to fuse together are more or less equivalent to the chemical reaction systems, while those in which fission is liable are comparable to the explosive type of reaction. While, therefore, the nuclei of the elements appear generally to be perfectly stable, actually they are in a metastable condition and, providing some activation energy is applied to them, more energy can be obtained

from them. One has to expend something before any results can be obtained. So far as the light nuclei are concerned a close approach of two of them should cause fusion with liberation of surface energy, but the positive charges of these nuclei usually prevent this, and it is only by some added outside energy that these repulsive forces can be overcome. Similarly, the heavy nuclei should break up with violent expulsion of energy, but they do not unless set into vibration by some outside source or unless a neutron or alpha particle is shot into them to cause upheaval within the nuclei.

The next question which has to be considered is—if some energy of activation is necessary, what is the magnitude of this energy in order to obtain the energy of fusion or fission? Again, reference must be made to the work of Bohr and Wheeler. So far as the light elements are concerned the matter resolves itself into a consideration of the products of the respective nuclear charges which means that with hydrogen nuclei whose charges are unity the activation energy is also proportional to unity but for oxygen with a charge of 8 the activation energy is 64 times greater. For the heavy elements where fission is to be produced a calculation of the activation energies necessitates taking into account the ba'ance between the electric propulsive forces on the protons and the forces of surface tension. As will be expected the greatest activation energy is required for those elements closest to silver and reduces very rapidly in the direction of the heaviest elements. When uranium is approached the activation energy required is only about 5,000,000 electron volts to produce an energy liberation of something of the order of 200,000,000 electron volts. But it should be pointed out that at the other end of the scale in order to obtain fusion only from half to one million electron volts is needed though admittedly the energy liberation is not of the same prolific proportions.

Speaking generally therefore it will be seen that the most advantageous elements for use as liberators of energy are those either at one end of the periodic table or the other. Those at the end of low atomic masses and charges give energy of surface tension while those at the heaviest end of the table with high positive charges produce energy by liberation of those charges while in the centre of the table in the neighbourhood of silver it is extremely difficult to obtain any advantage either way.

Earlier reference was made to two troublesome matters the first being the law of the conservation of matter with which we have dealt fairly thoroughly in the light of atomic science. The second of the two is the law of the conservation of energy. In its original form this law stated that energy could be neither created nor destroyed and the first experimental work carried out to prove this was performed by Joule in about 1845 but he was directly concerned with energy of heat or as it is always known the mechanical equivalent of heat. It has been necessary to refer to a considerable extent to energy expenditure and liberation in developing the explanation of the apparent loss of matter in accordance with equation 2 of Einstein's theory and it will now be readily understood that mass and energy are very closely interwoven. In fact, we can now refer to the mass-energy equivalent in much the same manner as we refer to the mechanical equivalent of heat.

Reference was made to the fact that in the make-up of the helium nucleus, or alpha particle apparently 0·028 units of matter are lost. But according to Einstein's theory, energy is equal to mass times the square of the velocity of light. If instead of the letter e for energy in equation 1, we write 933,000,000 electron volts, we have the energy equivalent for a mass of 1 or in other words the mass of the proton. If then we have a loss of 0·028 units this corresponds to a release of slightly more than 2,500,000 electron-volts which is a measure of the liberation of surface tension energy as a result of the input of upwards of 1,000,000 electron-volts. Here then, is the energy equivalent of apparent loss of matter.

Now we had occasion to make special reference to the first time that an atom had been split when it will be remembered that the lithium atom bombarded by a proton split up into two alpha particles. The accelerating voltage or activation energy was of the order of 600,000 volts, but the release of energy as a result of this splitting of the lithium atom is about 8,700,000 electron volts for each alpha particle or roughly thirty times the amount. It may be thought that here at any rate is the possibility of a source of abundant energy, but it must be remembered that by the means then adopted probably only one proton in 10,000,000 registered a hit on a lithium atom. The total amount of energy expended, therefore, was far in excess of that obtained by the one or two isolated results.

Before finally leaving this part of the subject, it will be of interest to consider what has happened when matter appears to be lost and in its place energy is gained. What form does this energy take? The answer is that it is the same form of energy as that referred to in Planck's Quantum Theory of radiation and is radiant energy or photons, to use the general name. If, therefore, energy of this nature can be released from matter, can radiant energy in the shape of photons or light rays, to use the more popular expression, have any effect on matter in the form of the nucleus of an atom? The answer is in the affirmative, and it is possible for nuclei of atoms to be disrupted by the absorption of radiant energy. Obviously this radiant energy must possess sufficient activation energy inherent in it before such a result could come to pass and in general cases no radiation possessing sufficient energy is available. But there is one instance in which the energy possessed by radiant energy is sufficient to cause the disassociation of nuclei and this is in the case of deuterium or heavy hydrogen, and it is quite probable that some time in the future this may prove to be of great benefit.

Perhaps the most fascinating point about the whole matter is, however, that it has been conclusively proved that radiation when passing close to nuclei will disappear as pure radiation and become material substance in the shape of electrons and positrons. The radiation which has been experimented with in this direction is of short wave-length, and is akin to if not the same as the gamma radiation which is expelled from certain radio-active sources. The fact remains that it does prove pretty conclusively that radiant energy which in its commonest form we term light is the ultimate source from which matter has probably been drawn. The atom was considered to be indivisible but is not so. The nucleus was also thought to be indivisible, but is a complex body, and the whole is merely the manifestation of energy in accordance with Einstein's equation relating energy, mass and the speed of light and this appears to be the most fundamental thing in the universe.

Hydrogen, Nitrogen and Oxygen in Ferrous Metals

Their Properties and Their Determination—Part IV

By E. C. Pigott

A very extensive literature exists on the gaseous constituents of irons, steels and ferro-alloys. Over a period of many years leading chemists and metallurgists have been engaged in piecing together the intricate facts brought to light. It would now seem that the main experimental and co-ordinating work has been done and that a clear perspective of this once totally obscure field has become possible. In the present article such a perspective is presented on the properties, extraction, and methods of determining the amount of oxygen present in iron and steel.

OXYGEN

At. Wt.—16·0000 (International arbitrary standard based on isotope O^{16}. Other isotopes, O^{18}, O^{17}).

M. Pt. —219° C.

B. Pt. —183° C.

S.G. Gaseous (air = 1·0), 1·105
Gaseous (hydrogen = 1·0), 15·87
Liquid 1·14
Solid 1·43

Wt. of 1 litre.—(N.T.P.), 1·429 g.

Solubility (100 vols. water, 15° C.), 3 vols.

Forms: Monatomic, diatomic, triatomic (ozone), tetratomic (oxozone).

Discovered in 1774 by Priestley.

Extraction

OXYGEN is the most widely distributed and the commonest of all the elements. It forms nearly 50% of the earth's crust, mainly as silicates and carbonates. Nearly one-quarter of the atmosphere consists of free oxygen, while water contains nearly 89% of combined oxygen. On the large scale, the atmosphere is the most practicable source, and virtually the whole of the oxygen of commerce is obtained by extraction from liquefied pure air on the principle of fractional distillation by processes such as that devised by Claude. The more volatile nitrogen boils off before the oxygen; on further evaporation the oxygen escapes, in entirety leaving behind liquid carbon dioxide and water. Claude oxygen contains 2–4% of nitrogen. Even where the fractional evaporation is repeated the product contains some argon (B.Pt. —186·1° C.).

Chemical Properties

Oxygen is a colourless, tasteless, odourless and non-combustible gas of great chemical activity. Air-oxygen mixtures containing one-third or more of oxygen readily re-ignite a glowing splinter. None of the three allotropic forms has any definite transition point, but they can exist simultaneously over a wide range, though in quantities varying according to temperature, pressure and the period of reactivity. At high temperatures both O_2 and O_3 produce free atoms of oxygen which can reunite into O_2. While the formation of O from O_2 is endothermic that of O from O_3 is exothermic.

Atomic oxygen, which is very unstable, is produced to the extent of about 20% when oxygen at low pressure (1 mm.) is passed through a silent electric discharge (0·25 amp.; 4,000 volts). It reacts in the cold with hydrogen, decomposes hydrocarbons (with the production of a bright bluish glow) and, owing to the great heat evolved when the oxygen atoms recombine, will melt platinum. Ammonia is oxidised, and even the very stable compound carbon tetrachloride.

Ozone, a pale blue gas having a strong characteristic smell, is generated in small proportions in many atomic oxygen-releasing reactions—e.g., when manganese dioxide reacts with cold concentrated sulphuric acid, and when moderately concentrated nitric acid is heated with ammonium persulphate. Ozonized oxygen containing up to about 10% of ozone is obtainable by means of the silent electric discharge. Electrolysis of ice-cold dilute sulphuric acid using a minute smooth platinum anode yields a concentration of 20–30%. Ozone boils at —112° C., and so can be effectively separated from oxygen (B.Pt. —183° C.) by fractional distillation. At room-temperatures the decomposition of ozone is slow, except in the presence of substances such as finely divided platinum, lead dioxide and manganese dioxide, which decompose it rapidly. It is also speedily reconverted into oxygen when heated to about 290° C., the conversion being exothermic. At much higher temperatures it is more stable, and its formation is facilitated owing to the initial production of the essential atomic oxygen. Ordinarily the solubility in water is 1% by volume; the aqueous solution exhibits many of the properties of ozone, but is unstable. It forms ozonides with many organic substances containing ethylene linkages—e.g., turpentine, benzene and rubber. The complete absorption of ozone in turpentine is utilised in the evaluation of ozonised air. Ozone is a very powerful oxidant: it deprives mercury of its lustre and spreads a film over the container walls; it liberates iodine from potassium iodide solution, but, unlike hydrogen peroxide, is without effect upon potassium permanganate solution. Ozone is blue-black when liquid and forms a dark violet crystalline mass when solid.

Oxozone, O_4 is present in highly ozonised oxygen.

Liquid oxygen is a bluish coloured, strongly magnetic liquid, which freezes to a pale bluish white solid with a S.G. of 1·426.

Gaseous oxygen combines to form oxides directly with most elements, particularly at elevated temperatures, and indirectly with all elements, excepting the inert gases. The order of reactivity with the metals is such that caesium combines most readily and platinum least

readily. The oxides of the elements are the most important of their compounds.

The conventional classification of oxides, while necessarily loose is, nevertheless, useful :—

Acidic oxides, those which combine with bases to form salts—e.g., CO_2, are oxides of non-metals, or of metal which can exert a high valency.

Basic oxides, those which combine with acids to form salts and water—e.g. CaO, CuO, are usually oxides of metals and are essentially the lower oxides.

Neutral oxides—e.g., H_2O, CO, N_2O, are those having no tendency to form salts either with acids or bases.

Amphoteric oxides—e.g., Al_2O_3, are those which behave either as acidic or as basic oxides, according to circumstances.

Peroxides—e.g., BaO_2 are, specifically, those which yield hydrogen peroxide when treated with dilute acids; or, more generally, the higher oxides.

The process of oxidation denotes an increase in valency of an element in its compounds with electronegative elements. The higher oxides of the metals are more volatile than the lower ones, since they tend to approach oxygen in their behaviour.

Many of the elements which form only basic oxides fall into groups I and II of the periodic table, while those which form only acidic oxides fall almost invariably into groups V, VI and VII. The amphoteric oxides tend to fall into groups III and IV.

Touching briefly on ordinary gas-analysis, it is seldom indeed that industrial gases are absolutely free from oxygen, which in almost every instance is introduced, intentionally or otherwise, in the form of air. Inherently, it is not detrimental to a gas, unless sufficient in quantity to carry an explosive hazard, but the fourfold volume of accompanying nitrogen is unwelcome. The presence of considerable quantities of oxygen is indicative of an air leak beyond the heated section of a plant or of the use of an excessive proportion of air for purification or for other purposes.

Detection by means of a feebly glowing splinter is applicable wherever the mixture under test contains more than about 30% of free oxygen. Nitrous oxide relights a strongly glowing splinter, but is readily distinguished by other tests. Oxygen is completely absorbed in alkaline potassium pyrogallate solution and this forms the basis of the usual method of determination in gases. For the Ambler and Bone-Wheeler types of apparatus 40% potassium hydroxide solution and 25% aqueous pyrogallol solution are mixed in the ratio of 4 : 1 as required. At 20° C. about 3 minutes' agitation is required for complete absorption; below 15° C. absorption is very slow. Another useful absorbent is Fieser's solution (16 g. $Na_2S_2O_3$, 6·6 g. NaOH, 2 g. sodium anthraquinone —β—sulphonate, 100 ml. water) which absorbs the oxygen far more readily than ordinary alkaline hyposulphite solutions, and obviates the need for vigorous agitation.

Consideration of Methods

The total oxygen is present in iron and steel as FeO Fe_2O_3, MnO, Al_2O_3, SiO_2, TiO_2, etc., and in various combinations of these oxides.

For the study of the state of combination, as well as of the shape, of oxide inclusions, the recognised method is that of direct microscopical examination of polished metal specimens, which may be aided by such identification means as etching with selective reagents, heat-tinting, and the use of reflected polarised light. The quantitative value of such practice is limited. Submicroscopic inclusions may occur in abundance, while of those microscopically visible, no more than an approximation can be found of their collective oxygen content. For these and kindred reasons, the precise determination of the oxygen content of the non-metallic matter necessarily calls for chemical methods of analysis. Some of these analytical methods available for the determination of oxygen in ferrous metals are suitable only for large well-equipped laboratories. The various methods may be classified into three groups :—

1. Vacuum-fusion gas extraction methods.
2. Residue methods, involving chemical isolation of the oxides and their microchemical or spectrographic examination.
3. Gravimetric methods, in which all the oxygen present is converted into alumina, or in which the water produced on reduction with hydrogen is absorbed.

The vacuum fusion method holds a pre-eminent position in that it is the standard against which the reliability of other methods is measured. Broadly, it has the advantages of low operative cost, comparative rapidity of operation, the use of large samples, and the important feature that hydrogen and nitrogen can be determined as well as oxygen. A disadvantage is the high capital cost. Residue methods do not suffer from this disadvantage and they reveal the distribution of the oxygen among the various oxides. The gravimetric aluminium method serves as one useful alternative to the vacuum-fusion process, like which it records not only oxide oxygen, but also any entrapped oxygen-bearing gases.

The hydrogen reduction process, originated by Ledebur, was the first method ever used in an attempt to determine oxygen in steel. It involves the passage of pure hydrogen over the sample at a temperature of 1,100°–1,200° C., the H_2O, CO and CO_2 being collected from the exit gases and their corresponding oxygen content measured. Very careful and skilful technique is essential. Even after many years of development and modification, application of the method is limited to materials containing only very small amounts of carbon, silicon and manganese. Peterson introduced the use of a catalyst in order to prevent the evolution of carbon monoxide. In 1936, Thompson and his collaborators found that at a temperature of 1,200° C., using an induction-heated Inver vessel, the results obtained on well-killed steels were in good agreement with those obtained by means of the vacuum-fusion method, provided that the iron oxide and alumina contents of the steels were not excessive. It was found that when applied to rimming steels the method gave erroneous results. A temperature of 400°–450° C. was found to be suitable for stripping the sample of extraneous surface oxide. One difficulty lies in obtaining refractory tubes that will yield a sufficiently low blank. In this respect transparent-silica tubes are far more stable towards hydrogen-reduction than translucent silica, porcelain, or fused alumina tubes.

Oxides in Pig Iron and Cast Iron

The microscopical examination of pig irons and cast irons for non-metallic inclusions does not disclose the amounts of FeO, SiO_2, MnO and Al_2O_3, because normally these are sub-microscopic in size. Usually, only sulphides and complex titanium inclusions are visible.

When the British Cast Iron Research Association embarked on the chemical estimation of the individual oxides in pig iron and cast iron, the alcoholic iodine and chlorine methods proved unsuitable; interference arose in the former from phosphorus and carbon, and in the latter, from manganese. The older acid methods were re-examined, but were found to have only a very limited application. Dilute acids had but a sluggish solvent action, while strong acids decomposed some of the silicates. A method based on the use of aqueous iodine was then evolved and adopted. (Taylor-Austin, Second and Third Reports of the Oxygen Sub-Committee; Iron and Steel Inst., 1939, 1941). However, the results obtained revealed such small variations between the amounts of individual oxides in different samples, and such a small total-oxygen content, that attention came to be directed to methods yielding merely a total oxygen figure, which is usually adequate. The vacuum-fusion method was acknowledged as unrivalled for this purpose, and the aluminium method of Gray and Sanders, which required little adaptation was also adopted. (Taylor Austin. Third Report of Oxygen Sub-Committee, Iron and Steel Inst., 1941, 328 p.).

Vacuum-Fusion Method

The accepted standard method for the determination of total oxygen in plain and alloy irons and steels and ferro-alloys is that of vacuum-fusion, a thoroughly reliable process which first occupied the attention of continental and American laboratories and which, during the past fifteen years, has been the subject of a great deal of development work in Britain, notably at the National Physical Laboratory. Provided certain precautions are taken the method yields accurate results not only for oxygen, but also for hydrogen and nitrogen on all classes of ferrous materials. When applied to reasonably homogeneous samples, the vacuum-fusion process is comparable in precision with that of other standard methods of chemical analysis. Reproducibility, even from one laboratory to another, is of a very striking order. The content range of total oxygen in clean, well-killed steels is about 0·002–0·03%, and the error is usually within ±0·0005%.

The sample is liquefied in a graphite crucible from which carbon rapidly enters the melt and converts the various oxides into carbon monoxide. An operating temperature of 1,550°–1,650° C. is customary. The crucible system is connected to a multi-stage mercury-vapour pump, which maintains a high vacuum of the order of 10^{-4} mm. above the surface of the melt. The gases are allowed to collect in a Töepler pump, from which they are transferred to a small gas-analysis apparatus. Normally, all the carbon monoxide is evolved within the first twenty minutes. It has been established that every one of the various oxides likely to be present in ferrous materials suffers complete reduction. Alumina and the complex oxides containing alumina are the most difficult to reduce, but if the vacuum is high even these respond to a temperature of 1,550° C. The basic oxides, CaO and MgO, which are not normally present in iron and steel to any extent, but which occasionally may occur in the form of entrapped slag particles, are exceptional in that they are not completely reduced. The amount of basic slag reduced at 1,600° C. (the usual operating temperature) is less than 50%, and even when the temperature is raised to 1,800° C., no more than 75% is reduced.

The chief drawback of the vacuum-fusion method is the length of time (2–3 hours) required for the preparatory degassing operation. Dismantling, cleaning and assembling are lengthy processes.

With iron and steel, the samples employed are solid cylinders, usually about 1 in. long and $\frac{3}{8}$ in. in diameter and weighing 15–20 g. Milled samples are unsuitable on account of their large surface area and consequent high surface-oxygen content. Surface oxidation, even of fresh millings of pure iron, may account for as much as 0·005% of oxygen.

Precautions are necessary when dealing with materials containing substantial amounts of the more volatile metallic constituents. Volatilisation results in deposition on the cooler parts of the reaction vessel of highly reactive metallic films, which adsorb the evolved gases. Of all the metallic elements commonly present in irons, steels and ferro-alloys, the most volatile is manganese. Molybdenum, copper, nickel and aluminium also tend to produce films, but by no means to the same extent. Once serious film-formation has commenced, the apparatus must be dismantled and cleaned. Except with volatile samples, such as irons or steels containing over 1% of manganese, six or eight samples may be reduced successively in the same crucible. Only a single sample of such materials as 12–15% manganese steel can be reduced before dismantling and cleaning.

In the examination of volatile steelmaking materials —e.g., aluminium metal, ferro-manganese, these are inserted into a bath of molten degassed iron or plain carbon steel many times the weight of the sample. Ferro-tungsten, the rate of film-formation of which is comparable with that of a high manganese steel, should also be diluted in a degassed bath. It would appear that the double carbide Fe_3W_3C decomposes into W_2C and vaporisable free iron, since melts containing over 30% of iron present no difficulty. Ferro-silicons and silicon-iron alloys should not be so diluted, since with these alloys a carbon-rich bath of iron sets up a sudden release of fine carbon and of a considerable quantity of gas.

Much of the fundamental work in this country on the vacuum-fusion method has been carried and at the National Physical Laboratory. A complete account of the very reliable method evolved there will be found in the Seventh Report on the Heterogeneity of Steel Ingots, pp. 82–95; (Iron and Steel Inst., 1937). The apparatus used yields a particularly low blank. Substantially, the apparatus and technique remain as then described, but it has since been found advantageous to raise the temperature at which gases are removed from the apparatus, and also to prepare the graphite powder surrounding the crucible by filing rather than by machining. (Eighth Report on the Heterogeneity of Steel Ingots, pp. 43–47).

Vacuum-fusion equipment devised by Stevenson and Speight consists of a water-cooled silica tube connected by a ground joint to a transparent silica head, and containing a graphite crucible and screens, heated by a 35kVA spark-gap high-frequency set. The vacuum is obtained by means of a three-stage gas-heated mercury diffusion pump, backed by a two-stage Hyvac oil pump, and the gases resulting from the reduction of the oxides in the specimen are collected by a Töepler pump of large capacity. Evacuation of the apparatus is carried out at 1,950° C. for 2 hours, to a pressure of 2×10^{-4} mm., and the base pressure at 1,600° C. is approximately 1×10^{-4} mm. A flexible metal connection is used between the furnace head and the mercury diffusion pump in order to

facilitate assembly of the apparatus. The analysis of the samples is conducted in a modified Orsat apparatus. A full description of the whole equipment and its operation will be found in the Seventh Report on the Heterogeneity of Steel Ingots, pp. 65–81. (Iron and Steel Inst., 1937).

A carbon-spiral type of furnace designed by G. E. A. Bramley and T. Raine also is described in the Eighth Report referred to above.

The method chosen for detailed description, in the present series of articles, is that devised by W. C. Newell of the Brown-Firth Research Laboratories. The essential features of his apparatus are a robust all-steel construction, high efficiency of the pumping equipment, comparative speed of working and automatic controls which simplify the mode of operation.

In so far as finished steel sections are concerned, the determination of oxygen holds certain advantages over microscopical examination. But it is at certain critical furnace stages that the determination is of most value. The traditional assessment of the state of oxidation of the molten steel on a basis of iron in the slag is indirect, and has other limitations. C. H. Herty early evolved a method in which spoon samples of the liquid steel are deoxidised with an excess of aluminium and in which the alumina is determined by chemical methods. In 1936, the method was improved by Kalling and Rudberg. The main problem is that of obtaining a representative sample of the bath. Another difficult problem is that of avoiding atmospheric oxidation, and many investigators have used evacuated containers. In the successful bomb-method (J. Iron Steel Inst. No. 2, 1943) a split bomb mould filled with a crumpled ball of aluminium wire is dipped into the bath and the cooled sample is forged down to 0·4-in. dia. bar for vacuum-fusion specimens or is drilled for the gravimetric or nephelometric determination of alumina ; the results are reliable and are obtained within thirty minutes.

Derge (Metals Technology, Jan., 1943), applies the vacuum-fusion method to a small rapidly cooled sample.

Fractional Vacuum-Fusion Method

Separation of the oxides and gases in irons, steels and ferro-alloys can be achieved by fractional extraction utilising the graded response of the constituent oxides to reduction by carbon ; a series of partial reductions is carried out, in the presence of tin, which functions as a flux, at progressively rising temperatures from about 1,080° C., whereby the oxides separate in the order FeO, MnO, SiO_2, Al_2O_3. The method was first described in 1933 by L. Reeve, who found that FeO is reduced at 1,050° C., MnO at 1,050°–1,150° C., SiO_2 at 1,300° C. and Al_2O_3 at 1,350°–1,600° C. Reeve's method has been investigated by Swinden, Stevenson and Speight (Second, Third and Fourth Reports of the Oxygen Sub-Committee). In practice some difficulty arises in separating the iron and manganese oxides, owing to the small interval between the melting point of the iron-carbon-tin alloy and the reduction temperature of manganese oxide. There is a tendency for the FeO, SiO_2 and Al_2O_3 results to be slightly low and for the MnO fraction to be slightly high. The accuracy is greatest where the inclusions are of a simple type—e.g., single oxides. The method has proved to be most successful with unkilled steels of the rimming type. Applied to weld metal deposits it has furnished very informative results. Theoretical objections to the method are the possible interaction in the presence of carbon and tin between the oxides and metals, and possible incomplete separation of the various oxides when they occur together. The volatility of the tin is such that only one sample can be reduced each time the apparatus is assembled, unless temperatures over 1,300° C. are avoided by resorting to a difference figure for alumina.

Electric Drive for Precious Metal Rolling Mill

ALTHOUGH much work is being done to increase and improve the facilities for rolling base metals, it is notewortuy that improved facilities are also being provided for rolling precious metals. A " Brightside " mill, for instance, installed at the works of the Sheffield Smelting Co., Ltd., for rolling gold and silver (fine and alloyed), and also nickel and copper, has recently been equipped by The General Electric Co., Ltd., with electric drive. The cast bars of material are reduced to sheets of varying thicknesses by cold rolling.

Showing the mill with a 200 h.p., 400-volt slipring motor, with reduction gears and mill pinions in one unit.

Particularly important, is the finish of the rolls, which must be capable of producing a flat, uniform sheet that is easily polished and free from surface defects. Cleanliness of the equipment and working area is also essential, in order to ensure that the precious metals handled are of the purity necessary to enable them to comply with Government assay tests prior to Hall Marking.

Chilled cast iron are used, 24-in. in diameter and 30-in. long, and the mill is driven by a 200-h.p., 400-volt slipring motor running at 585 r.p.m., but this speed is reduced by means of double helical gearing to about 10 r.p.m. The motor is mounted on top of the gear housing, which also incorporates the reduction gears and mill pinions. Forced feed lubrication is provided by means of a mechanical lubricator driven by a 1-h.p. protected type G.E.C. motor, which incorporates a safety switch.

Each bar of metal measures 12 in. × 5 in. × 1 in., and weighs about 20 lb., the mill handling 50 such bars per hour. Each stage of rolling reduces the thickness of the bar by approximately one-tenth, depending upon the type of metal being rolled, until a 50% reduction has been reached. The metal is then annealed. This sequence of operations is repeated until the desired gauge is reached.

ALUMINIUM——— and ITS ALLOYS

To meet Changing Problems and Domestic and Industrial Demands

ALTHOUGH the production and application of aluminium and its alloys, from a tonnage point of view, do not now reach the high levels experienced in the years 1943–45, the industry has been remarkably progressive in adjusting itself to peace-time conditions, with the result that applications of this metal greatly exceed pre-war tonnages. This progress does not mean that new alloys have been developed to create an increased demand; in fact, no completely new aluminium alloy of any commercial importance has been discovered during the last few years, practically all metallurgical activity has been directed to improving materials and techniques to meet the changing problems and demands of domestic and industrial applications. Rather is it that improvements in working the metal have been successfully applied over a wider range of products than before the war.

It is true to say that the outstanding progress achieved with this metal is largely due to the enormous strides which the development of modern transport has made —a development which has, on the one hand, caused engineers to explore all possible avenues for reducing weight, and, on the other, metallurgists energetically to search for new alloys or to improve existing ones Progress in the air has been particularly phenomenal, especially during the war period, when it became such a familiar material to those engaged in the aircraft industry that the number of people skilled in working it far exceeded those available in pre-war days. The fact that these skilled workers were available when the war ceased, together with the removal of restrictions on the uses of the metal, contributed considerably to greater peace-time applications. In addition, however, many materials were, and still are, in short supply and their applications controlled, whereas aluminium and its alloys are more freely available, in consequence they have in many instances displaced other materials and, while a reversal may take place when conditions change, aluminium will have had the opportunity to prove its usefulness for many applications previously denied it and in many cases will become a serious competitor of materials formerly used.

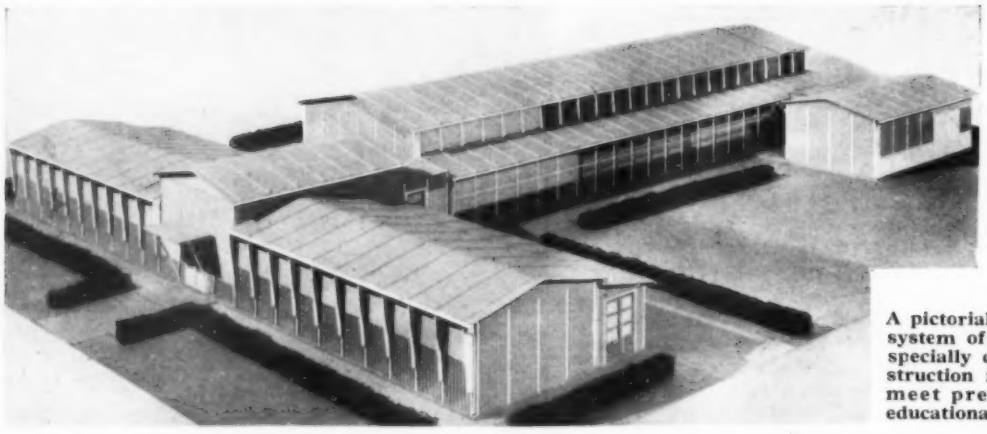
A comparison of present-day aluminium products with those available before the war shows that improved techniques, developed during the war have been applied in casting, rolling, forging, extrusion, pressing, drop-stamping, heat-treatment, welding and in finishing suitable alloys, to give results superior to those obtainable before the war. Since the war the use of aluminium has been extended to purposes for which it was previously uneconomic in competition with other metals and materials. Special and improved equipment has made practicable the production of structural shapes, heavy plates, forgings, tubing and sections in a wide range of sizes. Some of these manufactures are used instead of corresponding steel products for the assembly of structures, roof trusses of standard design, for instance, are now being manufactured. Round, square, oval and tapered tubing is currently made in a variety of sizes, while the complicated forms produced by the extrusion process are especially useful for architectural and structural purposes.

By courtesy of High Duty Alloys, Ltd.

An action shot showing the drop stamping of an aluminium alloy camshaft bracket. The stamping operation has been completed and the component is being removed to a clipping press to shear away the flash.

The most important industries in which aluminium products are applied include aircraft building and engineering; motor vehicles for road and rail; domestic utensils; chemical and electrical engineering; food and household appliances; furniture; textile machinery; railway carriages; mining; shipbuilding and marine engineering; containers for various purposes; dairy equipment; canning, etc. In diversity of uses, aluminium and its alloys compare with those of iron and steel. Their range of applications range from foil for packing to large shapes for structural purposes.

Among the most outstanding developments since the end of the war is that in which aluminium has entered into the construction of buildings. Pre-war applications were confined to windows, glazing bars, and various internal fittings, usually in buildings other than private houses. While aluminium-alloy glazing bars were used extensively in all types of building including factories and hospitals, window frames and other items of aluminium were found almost exclusively in hotels, banks, shops, offices, and other buildings of high standard. To-day, as a result of pre-fabrication, it has been applied successfully and economically to normal buildings;



A pictorial view of the unit system of school buildings specially designed for construction in aluminium to meet pressing needs of educational authorities.

some 40,000 aluminium bungalows, for instance, have been produced by the aircraft industry. And development in this field has not been confined to this country, figures published in the United States show that the amount of aluminium now used in building is greater than in any other industry, including transport.

Two years ago it was stated* that of all the manifold domestic problems left us by the war, none were more urgent than that of building, and it was urged that aluminium could span the transitional period. It was emphasised, however, that real expansion of the uses of aluminium in ordinary building depended upon a plentiful supply of all building assemblies and hardware in aluminium, via the normal channels, in forms which the builder could use without studying scientific theses, from roof-truss assemblies to the humble wood screw. To-day the position is that aluminium as a roof covering is well established as weathering to flat or pitched roofs, sheet tiles. Aluminium alloy roof trusses are built up from sections either extruded or formed strip. Windows are in large scale production from wrought stock and as castings. In addition, window surrounds and fittings of aluminium are now used. Gutters and all rainwater goods are available either in the form of castings or pressings from sheet. It is noteworthy that a British standard for rainwater goods in aluminium will be issued shortly. Many fittings, normally classed as builders' ironmongery and hardware, are in production, including door furniture, skirtings, picture rail and lighting fittings. Sinks and draining boards, complete with supports and splash backs, are made either as castings or fabricated from wrought material. In addition, many building appliances in aluminium, such as ladders, scaffolding and shuttering, have been developed and show substantial economies in use.

A further development in this field is the aluminium unit construction for school buildings demonstrated to Local Education Authorities and other bodies, faced with the problem of erecting school buildings, at a recent Exhibition held in London. The system adopted is designed to reduce the use of controlled materials to a minimum and to provide pleasant and permanent school buildings at an economic price. This system of unit construction, shown in the accompanying illustration, is the result of collaboration between the engineers and technicians of the Bristol Aeroplane Co. (Housing), Ltd., the consultant architects retained by the Company, and the Northern Aluminium Co., Ltd. When fully developed the units will give a maximum range of school building, from staff rooms and lavatory units to two-storey class-room construction.

Transport Industries

While the industry has given considerable attention to developments in application in connection with building, much progress has been made in almost all other industries and undoubtedly the most important is that concerned with transport. The reduction of dead load in transport vehicles by the use of aluminium was appreciated before the war as having considerable economic advantages. The exigencies of war curtailed applications in this direction, apart from aircraft, but, during the last two years, domestic as well as overseas requirements for road and rail vehicles have increased the use of aluminium and the consumption in this field far exceeds that applied before the war. The bodywork of nearly all buses consist mainly of aluminium materials. For the road transport of goods, especially when covered vans are employed, there has been a substantial increase in the amount of aluminium used. A more recent development is the use of aluminium in mining equipment and aluminium coal trams are now in use complete with wheels, axles and shackles.

The reduction in dead load by the use of aluminium in shipbuilding is well known. Ships lifeboats, motor boats of various kinds, superstructures, funnels, ships fittings, as well as many engine parts, have been successfully made in suitable aluminium alloys. In this connection the recent issue by Lloyds Register of Shipping of tentative requirements for the quality and testing of aluminium alloys for shipbuilding purposes is very significant. For parts which are continually exposed to sea spray, alloys must be chosen which possess suitable qualities, whilst other considerations like weight saving and paint adherence also enters into account. The use of suitable aluminium alloys is being applied to davits, derricks, ventilators, and many similar applications such as searchlight parts, portholes, grilles for lift enclosures lockers and partitions. In the engine room too, aluminium and its alloys are winning a place on their merits and such parts as gear casings, engine bedplates, crankcases, floor plates, air ejector covers, lubrication pumps, end brackets for electric motors, pistons for diesel

Contd. on page 194

* "Aluminium and the Building Programme," by George Mortimer, *Metallurgia*, 1946, **33**, 189–192.

Light Alloy Piston Materials

By A. Schofield* and L. M. Wyatt, M.A., A.R.I.C.†

It is probable that internal combustion engine pistons are subjected to more severe service conditions than any other component. It is not surprising, therefore, that considerable research and experience have been necessary to develop the most satisfactory materials for their production. No one metal or alloy fulfills all the requirements for this application, but experience has shown that suitable aluminium alloys combine a greater number of desirable features, although, as will be noted in this paper, the selection for a comparatively narrow field necessitates a compromise of desirable properties.

BY far the larger proportion of pistons used in the world to-day is made from one of the aluminium alloys. This component probably represents the most severe application of these alloys, but experience has shown that certain alloys have a combination of properties which make them particularly suited to this purpose. A list of these alloys is given in Table I, together with an attempt to show the relationship between the various names applied to what are basically similar alloys.

TABLE I.—PISTON ALLOYS

Alloy type		England		Germany		America	
		Cast	Forged	Cast	Forged	Cast	Forged
Al/Cu		L.8 No. 12 L.11 B.101 LAC.10	B.101				Lynite No. 12 SAE.34
Al Cu Ni Mg	Y	"Y" alloy L.24 L.35	"Y" alloy L.25 SL.102				188
	RR	RR.53 DTD.238 RR.53C ceralumin	RR.58 RR.59 L.42 ceralumin				
Eutectic silicon		Lo-Ex S.132 SM.116	DTD.324 SL.101	EC.124 Kupfer silumin KS.245	EC.124 KS.1275	Lo-Ex 132	388
Hyper eutectic silicon				KS.280 Alusil Supra Kolben	EC.138		
L.40 type R.A.E.		L.40 (?) R.A.E.55 R.A.E. 40C	R.A.E.55 R.A.E. 40C				
Medium silicon type		SAE.300				A.355 S.A.E.300	

It is well known that pure aluminium, although possessing excellent conductivity and low specific gravity, is too soft to be used for any but the most lightly stressed applications; the development in the application of aluminium, however, has progressed rapidly with the addition of elements which increase the hardness at the operating temperature and reduce the coefficient of expansion without reducing too much the conductivity and other useful properties of the pure metal. The elements commonly used for this purpose are copper, silicon, magnesium, iron, nickel, manganese, zinc, titanium, cerium, columbium, molybdenum and boron.

Copper is the most effective in hardening, and a hardness of 130 BHN can be achieved by the addition of copper alone. Silicon is probably the second most important element in light metal piston alloys. It is

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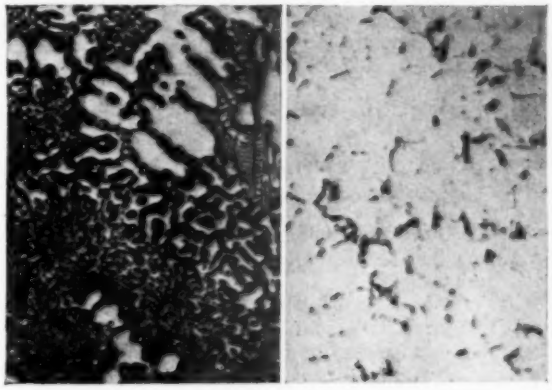


Fig. 1.—Structure of aluminium-silicon alloy. Structure of aluminium-copper alloy.

not taken into solid solution to a large extent and alloys containing silicon have very different structures from those in which copper is the alloying element. Fig. 1 shows for comparison the structures of an aluminium-silicon alloy containing 13% silicon and an aluminium-copper alloy containing 6% copper. Silicon has not nearly the hardening capacity of copper, but it has considerable influence in reducing the thermal expansion of the metal. It also increases the castability and reduces the tendency to hot shortness. Even when present in small quantities, however, it accelerates the tendency of copper, present in the alloy, to come out of solution. When present in combination with magnesium it forms Mg_2Si. This constituent has great age-hardening properties, but the hardening occurs at a lower temperature than the alloys with copper and those alloys which rely mainly on Mg_2Si for their hardness have very poor hot strength.

Magnesium hardens aluminium by forming a solid solution which is not affected by heat-treatment and consequently has high hot hardness, but low creep strength. It also increases the tendency of copper to come out of solid solution. High magnesium-containing alloys, however, are difficult to cast and forge, have very low creep strength, and, being solid solution alloys, have very poor thermal conductivity.

Iron, nickel and manganese all occur in aluminium alloys as small hard intermetallic particles which contribute some hardening effect and a decrease in ductility. Iron greatly reduces the age-hardening capacity of copper-aluminium alloys by forming a ternary compound (0·1% of iron is equivalent to a loss of 0·3%

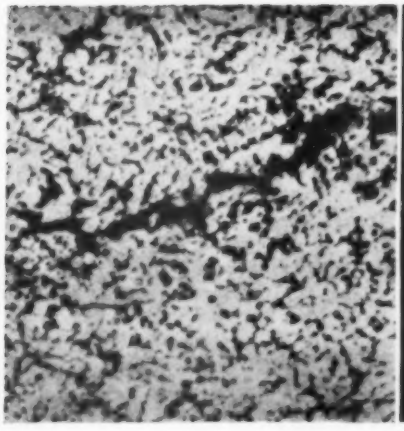


Fig. 2.—Hot tear. × 100.

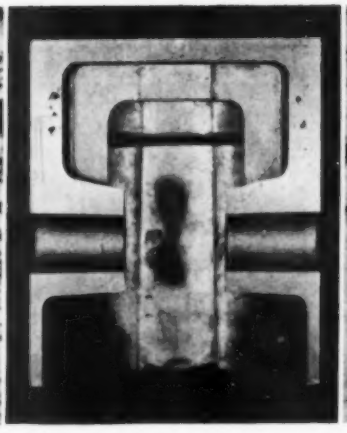


Fig. 3.—Coarse shrinkage.

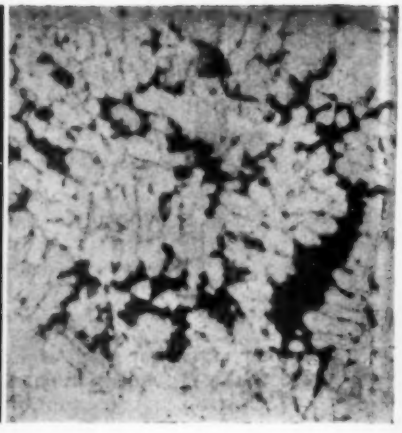


Fig. 4.—Fine shrinkage. × 100.

copper in this respect) and, when present in a quantity of approximately 0·8% and over, retards the tendency of an alloy to spontaneous age-hardening at room temperature. Manganese has a considerable strengthening effect on the copper-bearing alloys but is seldom added to piston alloys. The hardening effect of nickel is believed to persist at high temperatures and this metal is used in a great many piston alloys. The total percentage of iron, manganese and nickel in an aluminium alloy is limited by considerations of castability and ductility. The manganese content is, therefore, kept as low as possible in order to accommodate more of the "hot strength" element, nickel. Iron is considered to have an influence in restraining grain growth during heat-treatment, but its effectiveness has not, in the authors' experience, been very marked.

Titanium, cerium, or columbium are frequently present as grain refiners. The authors have experience of the particular effectiveness of boron as a grain refiner and titanium as a grain growth inhibitor for heat-treated forged alloys. Molybdenum[1] is used occasionally in amounts up to 0·3% as a grain refiner, but as it is less effective than titanium, it is used mainly for patent reasons. Zinc has a very considerable age-hardening capacity, particularly in the presence of magnesium. Aluminium-zinc-magnesium alloys, however, age harden and soften at comparatively low temperatures and zinc is consequently never used in piston alloys.

In addition to the elements intentionally added, traces of various metals such as cadmium, chromium, lead, tin, zinc, etc., are also present. The iron and silicon content of virgin aluminium varies from 0·003–0·8% or even more, and the cost of aluminium increases as the quantities of these impurities decrease. Secondary metal is liable to contain all these and other residuals, particularly manganese derived from duralumin, the most widespread source of secondary aluminium.

1 "Metallography of Aluminium Alloys," by Mondolfo, p. 31. (The book is the latest and most authoritative work on the alloying constituents of aluminium alloys).

Choice of a Piston Alloy

In choosing a piston alloy, it is first necessary to decide whether low cost, strength at high temperatures, thermal conductivity, bearing properties, or low coefficient of thermal expansion, is the most important factor. For low cost, an alloy would be chosen giving wide ranges of composition of the greatest number of elements, taking particular care to include manganese, iron and silicon, so that it could be made from general scrap. Sufficient copper and silicon could then be added to harden the alloy and to increase its castability.

If strength and castability are required to be the most outstanding properties, copper, magnesium and silicon are the predominating elements to which are added iron

TABLE II.—COMPOSITION OF TYPICAL PISTON ALLOYS

	Casting Alloys								Wrought Alloys			
			Copper alloys			Al-Cu-Ni-Mg type		High Si alloy		Al-Cu-Ni-Mg type			High Si alloy
Composition	S.A.E. 300	L.40 type alloy	LAC.10	L.11	Al-Cu alloy	Y	RR.53	Lo-Ex	KS.280	Y	RR.59	RR.58	DTD.324
Cu	% 7·0	% 2·0	% 9·5	% 7·0	% 6·0	% 4·0	% 2·2	% 1·0	% 1·5	% 4·0	% 2·2	% 2·2	% 1·0
Ni	0·2	1·8	0·2	—	—	2·0	1·2	1·0	1·5	2·0	1·2	1·2	1·0
Mg	0·3	1·0	0·25	—	—	1·5	1·5	1·0	0·5	1·5	1·5	1·5	1·0
Fe	0·6	0·5	0·5	0·4	Fe + Si 0·1 max.	0·3	1·1	0·55	0·5	0·3	1·0	1·0	0·55
Si	5·5	0·5	0·55	0·4		0·3	1·6	11·5	21·5	0·3	0·6	0·1	11·5
Mn	0·4	1·0	0·4	Sn 1·0	Small amount of Grain refiner	0·2	0·05	0·3	0·7	0·2	0·05	0·05	0·03
Ti	Trace	Grain refiner	Trace	0·05		Trace	0·07	0·025	Co 1·2	Trace	0·08	0·08	0·025
Al	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance

Fig. 5.—Shrinkage shown in piston (Sink).

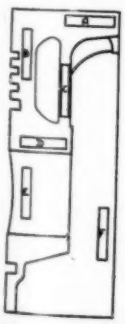
and nickel up to a total of 2% together with a grain refiner. For high-temperature strength, the silicon, and possibly the iron, would be reduced to the lowest possible value and the copper content increased considerably. For a low coefficient of expansion an alloy with a high silicon content would be needed with sufficient copper, nickel and magnesium to give the necessary hardness.

Table II shows the composition of ten alloys generally used for pistons,[2] distinguishing between cast and wrought alloys and which illustrates the considerations mentioned in the previous paragraphs.

Fabrication

All the methods of piston fabrication used involve the casting of the alloy, either in its finished form or as a billet, and the production of the complicated shapes required by

2 Cast Lo-Ex often has 2·4% Ni, but we have found the 1% Ni composition to be superior and, in this, we agree with German practice in EC. 124.



TEST BAR POSITION		SAND CORE	GRAVITY DIE CAST	PRESSED CAST STOCK	PRESSED PRE-WORKED
A	TOP	12·0	16·0	25·0	27·5
	BOTTOM	1·0	1·5	3·0	5·0
B	TOP	13·0	16·0	23·0	28·5
	BOTTOM	1·0	1·5	2·0	5·5
C	TOP	14·0	16·0	26·0	28·0
	BOTTOM	1·0	1·5	4·0	7·5
D	TOP	16·0	16·0	24·5	28·0
	BOTTOM	1·5	1·5	3·5	5·0
E	TOP	17·0	18·0	26·0	28·0
	BOTTOM	1·5	2·0	5·0	9·0
F	TOP	19·0	19·0	26·5	29·0
	BOTTOM	2·0	2·0	6·0	11·0

Fig. 6.—Strength of pistons against method of manufacture.

piston design results in a modification of the properties of the alloys.

The more important defects which occur are fundamental characteristics of the metal due to the contraction during and after solidification, examples are shown in Figs. 2–5. Table III shows which alloys are most susceptible to each class of defect—also which alloys develop a coarse structure during slow solidification. From this it can be seen which alloys are most suitable for the alternative piston manufacturing processes.

TABLE III.—SUSCEPTIBILITY OF ALLOYS TO CERTAIN DEFECTS

Alloy	Resistance to				
	Hot tear	Coarse shrinkage	Fine shrinkage	Sinks	Coarse structure
RR.59	8	1–6	4, 5 & 6	7	1–5
Y	7			6	
RR.53	6			5	
L.11	5		7	2	
LAC.10	4		8	1	7 & 8
SAE.100	3			8	
KS.280	2	8	1, 2 & 3	4	
Lo-Ex	1	7		3	6

When conditions of service necessitate exceptional properties and maximum consistency it is better to forge the piston from stock which by reason of its shape can be cast both sounder and more consistently. Such high-quality stock can best be produced by continuous casting or equivalent methods. Fig. 6 shows the variation in properties of a "Y" alloy piston made in different ways.

Heat-treatment

The mechanical properties of most of the piston alloys are developed by heat-treatment, and this is one of the most important factors in piston production. Not only should the maximum possible hardness and fatigue strength be obtained, but, in addition, pistons should be free from internal stress induced during manufacture and constant in dimensions both during machining and running. These requirements are to some extent mutually exclusive, and it is desirable to obtain the best compromise possible.

Three factors which can be varied are time and temperature of solution, severity of quench, and time and temperature of precipitation hardening. Severity of quench is probably the most critical feature of all,

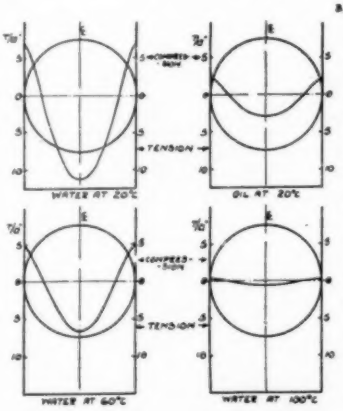


Fig. 7.—Stresses induced in 3 in. "Y" alloy cylinder by quenching from 510° C. in various quenching media.

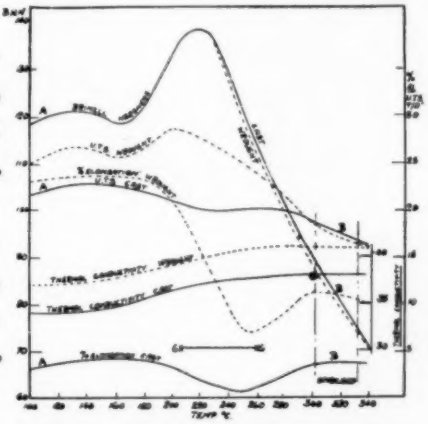


Fig. 8.—Properties of "Y" alloy quenched in boiling water after 2 hours precipitation at different temperatures.

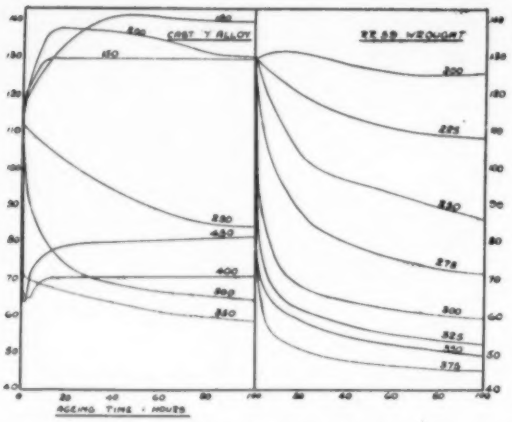


Fig. 9.—The relationship between the hardness of fully heat-treated "Y" alloy and RR. 59 and the time and temperature to which they have been subjected.

the more rapid the cooling the greater the hardness and better the mechanical properties, but too rapid a cooling may produce a considerable stress in the material. Fig. 7 shows the stresses induced in a 3-in. diameter cylinder of "Y" alloy quenched in various ways.[3] Boiling water has been found to be the best quench medium for most pistons.

Fig. 8 shows the effect of various precipitation heat-treatment temperatures on continuous cast and forged "Y" alloy which has been solution heat-treated and quenched in boiling water. G-G shows the range over which growth occurs in an alloy subject to it.

Increasing the temperature at which a chemical reaction takes place by 10°C., approximately doubles its velocity. For example 2 hours at 180° C. is equivalent to 4 hours at 170° C., 8 hours at 160° C., and so on. Thus, a precipitation treatment of 2 hours duration can generally be used.

A convenient heat-treatment for "Y" alloy, and one which produces a suitable hardness with a reasonable ductility, consists in leaving it for 4 hours in the boiling quench tank after quenching. For very large pistons, which attain very high temperatures in the crown,

3 For methods of determining residual stresses and references to work done, see "Practical Metallurgy," by Sachs, p. 179.

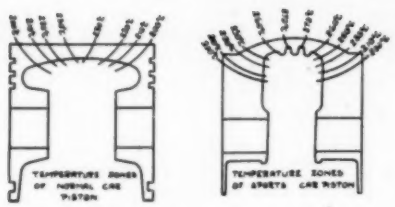


Fig. 10.—Temperature distribution in a Lagonda piston.

precipitation is carried on much further so that the piston hardens to 80 Brinell and corresponds to point "B" on the curve.

Service Conditions

Service temperature conditions of used pistons can best be estimated by "recovery hardness" or etching colour methods. Fig. 9 shows the relationship between the hardness of fully heat-treated "Y" alloy and RR.59 and the time and temperature to which they have been subjected. By means of these curves and within the range covered by them the temperature attained at any point of the piston can be estimated by recovery hardness if the running-in time is known.

Temperature distribution in the Lagonda piston shown in Fig. 10 is typical of a high-duty sports car engine. The working parts of the piston are well below the dangerous temperature of 230° C. In consequence, such a piston can be made very satisfactorily from a high silicon type of alloy. In the diesel engine piston on the other hand, temperature has to be considered very seriously. The temperature distribution in a large size diesel of the Ricardo "Comet" type is shown in Fig. 11.

The temperature distributions which can occur in a rather difficult type of transport diesel engine are shown in Fig. 12. This engine sets the piston designer a problem because of the close proximity of the combustion chamber to the gudgeon pin boss and ring grooves. The two illustrations show the effect of running conditions on the piston. The piston at "A" has been used under normal conditions and will give satisfactory service for an indefinite period. Unusually severe conditions, such as ignition mis-timing, incorrect governor setting or ineffective cooling may lead to a temperature distribution as at "B." This can lead to failure of the piston because the working portions are at the temperature (230° C.

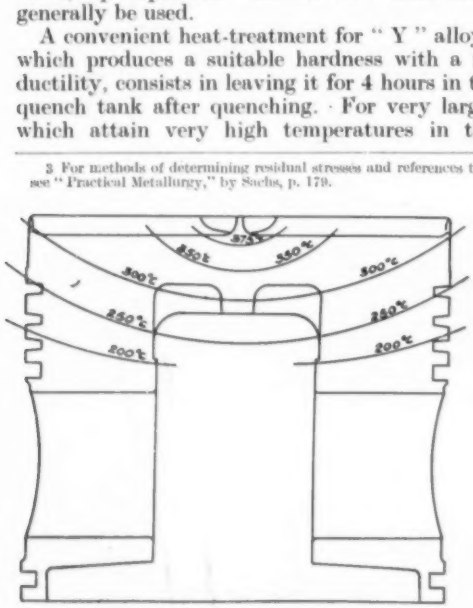


Fig. 11.—Temperature distribution in a large-sized diesel piston of the Ricardo "Comet" type.

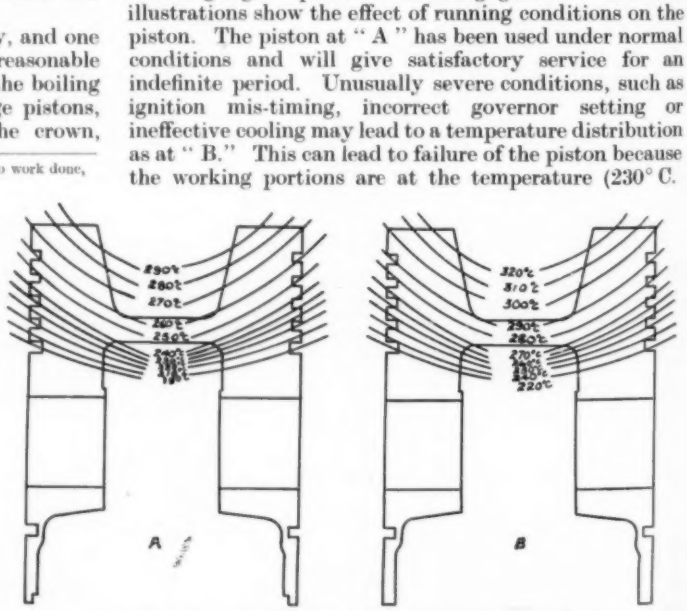


Fig. 12.—Temperature distribution in a difficult type of road diesel piston. A. Correct. B. Incorrect.

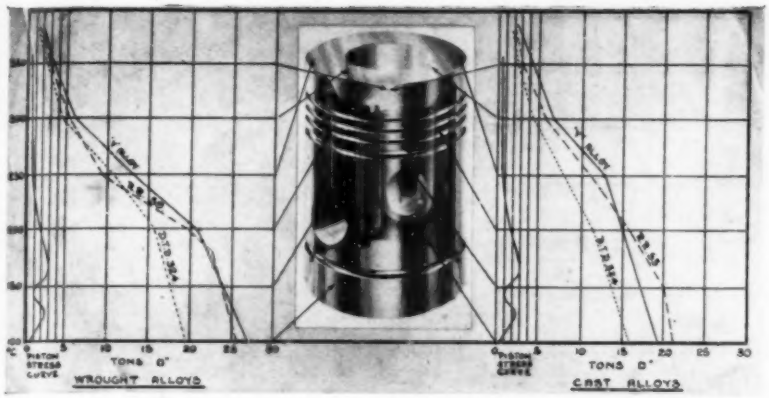


Fig. 13.—Comparison of cast and wrought alloys at piston-operating temperature with actual stress in a piston.

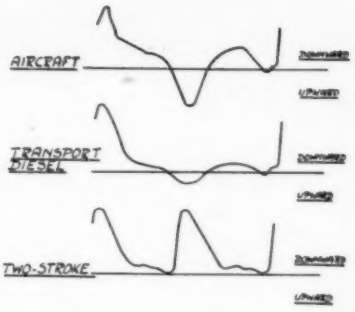


Fig. 14.—Variation of gudgeon pin load with time.

at which softening of the age-hardenable alloys commences.

The essence of good piston alloy development is to keep the softening temperature of the alloy as high as possible while retaining the necessary high-strength properties at lower temperatures.

Actual piston failures in the high-temperature areas are infrequent and nearly always caused by thermal stresses. For resistance to these a high thermal conductivity, low thermal expansion and high elongation value are more important than hot strength and therefore, strength at very high temperatures is not of paramount importance and design should aim at preventing this occurrence. Failures normally occur in the cool areas of the piston, particularly if the 239° C. region approaches the highly stressed portions.

The results of these stress determinations for a transport diesel type of piston are shown diagrammatically in Fig. 13 containing also the hot strengths of typical cast and wrought piston alloys. This property of hot strength, which is more properly defined as "tensile strength at elevated temperatures at a high loading rate after heating for 50 hours," has been found to be the most useful property for assessing the relative merits of piston alloys, from the points of view of fracture, deformation and seizure. As can be seen from the illustration, it does not bear a direct relation to the failing load on a piston, although it does show the advantages to be gained by the careful choice of alloys in this respect.

The different types of load to which the gudgeon pin boss regions of typical pistons are subjected are shown in Fig. 14. In the case of the first example, the fatigue component of load is considerably more important than the creep component, whereas in the third example the creep component is very much more serious than the fatigue. In the second example, which is intermediate, analysis of the stress pattern will show that the region round the boss, subjected to the inertia load and the flexure of the gudgeon pin, will undergo a considerable fatigue loading with very little creep component; on the other hand, the region above the boss which withstands the gas load will have to resist a load consisting mainly of creep stress.

Mechanical Properties

Combined creep and fatigue.—Fig. 15 gives the range of combined tensile creep and fatigue load withstood at 200° and 300° C. of typical wrought alloys. The results are worthy of careful study because they show wherein lies the superiority of the Al-Cu-Ni-Mg group of alloys represented by "Y" alloy. The other alloys are not so much inferior in fatigue strength to "Y" alloy, but the admissible range of combined creep and fatigue is very much smaller.

In Fig. 16 a cast alloy is compared with the same alloy in the wrought condition. The cast alloy is superior

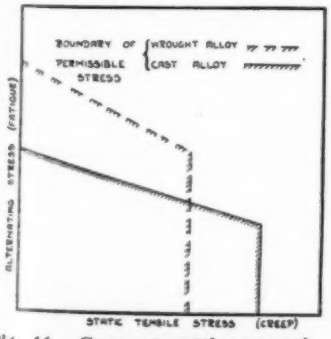


Fig. 16.—Creep strength comparison of cast and wrought alloys.

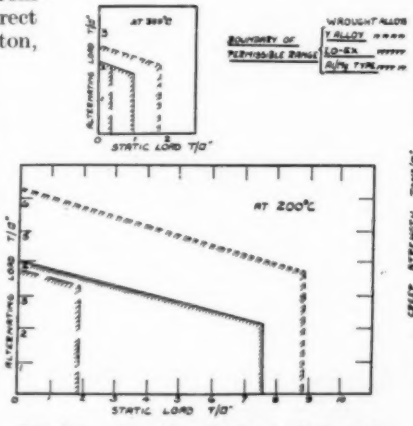


Fig. 15.—Combined alternating and static stress tests.

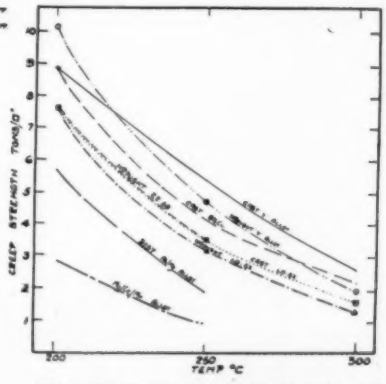


Fig. 17.—Creep strength of cast and forged alloys, DVM method.

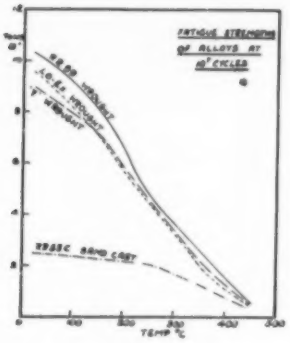


Fig. 18.–Fatigue strengths of some typical alloys at 10^7 cycles.

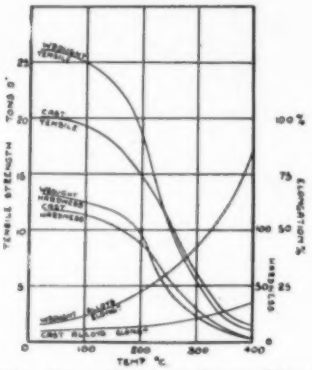


Fig. 21.—Comparison of hot strength of cast and wrought alloys.

Fig. 22.–Piston pressed from cast blank.

in resistance to creep, while the forged alloy has a much greater fatigue strength. This difference in properties is of great importance in the choice of a piston material.

Creep strength.—The creep strengths of most of the cast and wrought alloys have been determined and Fig. 17 shows the variation in this property with temperature.[4] The superiority of the cast alloys and the excellent creep resistance of " Y " alloy is apparent.

Fig. 18 shows the fatigue strengths of three of the wrought alloys and a sand-cast alloy. This clearly shows the advantage of the wrought alloys in this respect. Typical fatigue-strength values of cast " Y " alloy and LO-EX are plus and minus 7 tons/sq. in. and 6 tons/sq. in., respectively. In general it may be said that the Al-Cu-Ni-Mg alloys show the best fatigue properties throughout the range. Die-cast alloys are superior to sand cast in fatigue, but still considerably inferior to wrought alloys.

Hot strength and hardness.—The hot strength and hardness of the alloys is a good guide to their properties provided that :—

(*a*) The loading is applied at a known and constant rate.

(*b*) The alloys are soaked for a sufficiently long period before testing.

4 " Prufung and Leichtmetallen bei hoherer Temperatur," by Karl Wellinger und Eust Keil. (Note the RR. 59 had 1·67% Fe, but otherwise conformed to specification).

The results[5] illustrated in Figs. 19 and 20 have been obtained with a loading rate of 20 tons/sq. in. per min. after 50 hours soaking time. They place the alloys in much the same order as the fatigue and creep tests already quoted, and it does seem that a pretty fair idea of the fatigue strength can be obtained over the temperature range by taking it at about 30% of the tensile strength.

A comparison between the hot strength of an alloy in the wrought and in the cast state is given in Fig. 21, in which the percentage elongation and the hot hardness are also shown. The superiority in hot strength of the forged alloys at temperatures below 230° C. is strongly marked, while the castings show to advantage above this temperature.

Recovery hardness.—At high temperatures the recovery hardness is very closely related to the hot strength, and it is possible to deduce the hot tensile strength of an alloy at 300° C. and at 350° C. from the relations :—

Recovery Brinell (300° C.) − 20 = 8 × Hot tensile strength (300° C.).

Recovery Brinell (350° C.) − 20 = 10·2 × hot tensile strength (350° C.).

Consideration of the mechanical properties of the materials indicates what alloys and methods of fabrication are most suited for each type of piston.

The most favourable methods are :—

Aircraft piston.—Pre-worked wrought Al-Cu-Ni-Mg type alloy.

Large diesel.—Cast Al-Cu-Ni-Mg (preferably "Y" alloy).

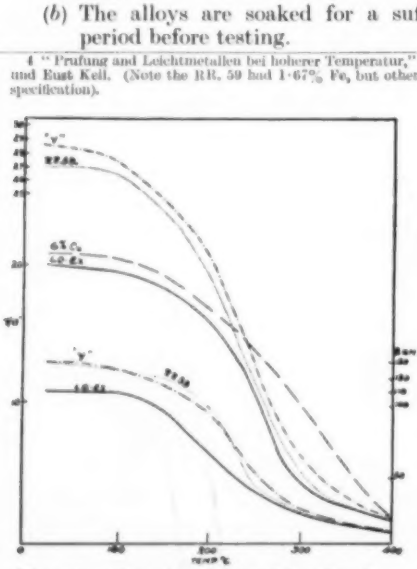


Fig. 19.—Hot strength and hot hardness of wrought alloys.

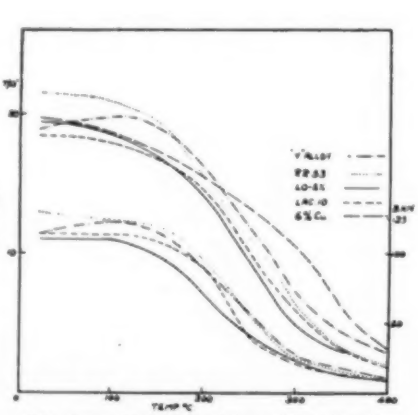


Fig. 20.—Hot strength and hot hardness of cast alloys.

5 Results quoted from work by the authors on compositions are given in the original paper. The best comparative work is given in : (*a*) The "Metals Handbook" of the A.S.M., pp. 1,268, 1,275, 1,283 ; (*b*) unpublished work of the B.N.F.M.R.A.

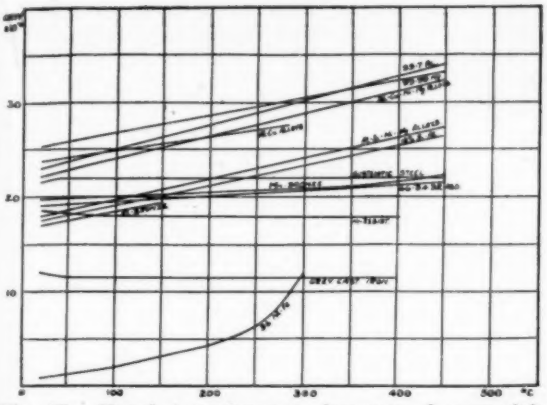


Fig. 23.—Showing tendency to increase of expansivity with increasing temperature of several metals.

High-duty car.—Wrought low-expansion alloy.

Low-duty car (where cost is major consideration)—Cast low-expansion alloy.

Transport diesel.—Pressed from cast blank in low expansion or Al-Cu-Ni-Mg alloy.

TABLE IV.—SPECIFIC GRAVITIES OF MOST COMMONLY USED ALLOYS

Alloy	Max.	Min.	Average
"Y"	2·82	2·77	2·80
RR. 53	2·80	2·75	2·78
Lo-Ex	2·80	2·75	2·78
LAC. 10	2·93	2·89	2·92
L. 11	2·89	2·85	2·87
KS. 280	2·70	2·66	2·68
SAE. 100	2·86	2·80	2·83

	"Y" Alloy						Calculated S.G.
	Cu	Ni	Mg	Fe	Si	Mn	
Most dense ..	4·5	2·3	1·2	0·6	0·3	0·3	2·83
Least dense	3·5	1·8	1·7	0·3	0·6	—	2·77

An example of this latter form of fabrication is shown in Fig. 22. Such a piston combines the high-creep strength of the cast alloys with the consistency, high-fatigue strength and thermal conductivity of the wrought in the most advantageous positions for each property.

Physical Properties

Specific gravity.—The specific gravities of the most commonly used alloys and the calculated and observed specific gravity possible with "Y" alloy at its least dense and most dense compositions are shown in Table IV.

Thermal expansion.—If the specific gravity can be calculated with such accuracy, it also follows that the coefficient of thermal expansion should also be calculable. Thus, by including metals of low coefficient of thermal expansion, the coefficient of thermal expansion of the alloy can be lowered.

The coefficients of thermal expansion[6] of the light alloys and other commonly used metals are shown in Fig. 23. Fig. 24 shows the clearance required in a 4½-in. diameter piston for various piston alloys in grey cast iron or austenitic cast-iron liners. These

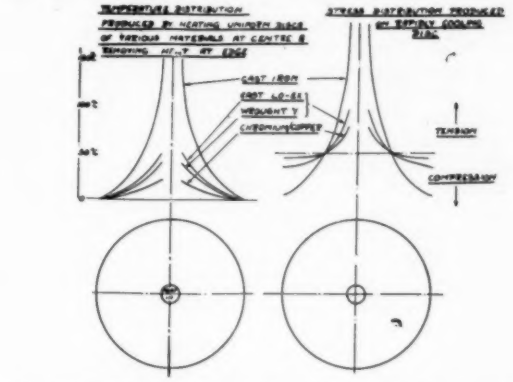


Fig. 26.—Effect of thermal conductivity and expansion on performance.

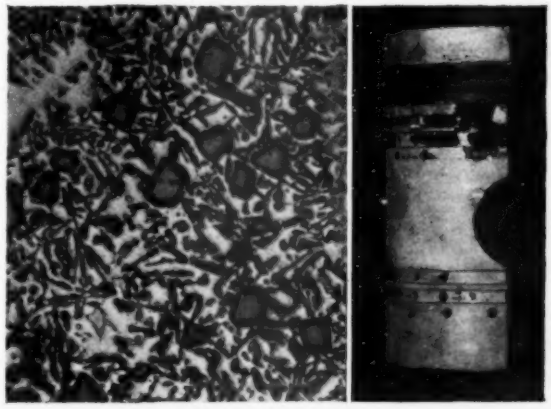


Fig. 27. Fig. 28.

Fig. 27.—Showing the structure of the high silicon alloy KS. 280. Fig. 28.—Austenitic cast iron ring carrier insert in a London bus piston after 90,000 miles service.

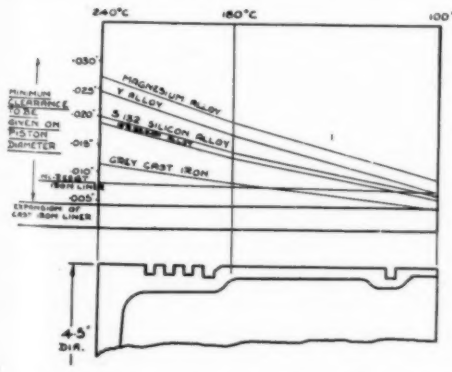


Fig. 24.—Piston clearances for different alloys.

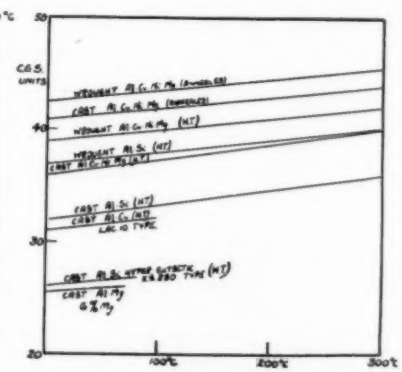


Fig. 25.—Thermal conductivity of aluminium piston alloys.

6 Authors' results quoted in most cases, but should be quoted with: (*a*) M.A.P. Scientific and Technical Memo. C1/42; (*b*) Hiduminium Technical Data—High-duty Alloys, Ltd., Slough; (*c*) A.S.M. Metals Handbook; (*d*) Metallurgy of Aluminium and its Alloys by, Zeerleder.

figures demonstrate the advantages of the aluminium silicon alloys.

Thermal conductivity.—The thermal conductivities of cast and wrought alloys in the fully heat-treated and annealed states are shown in Fig. 25. All the best piston alloys have thermal conductivities in the region of 0·32–0·45 c.g.s. units. The success of these alloys as piston materials has probably been due partly to their high thermal conductivities. Wrought alloys are superior to cast alloys in regard to thermal conductivity.

The influence of thermal conductivity on performance is illustrated in Fig. 26, showing the comparative temperatures which would be attained in a piston crown of uniform thickness, were the whole of its heat to be absorbed in the centre and dissipated on the outside edge, a condition which is approached by some pistons. On the same figure is shown the approximate stress distribution which would be produced on rapidly cooling such a disc which had " stabilised " itself at the temperatures shown.

Type of surface	Load (lb./in.)	Time before Seizure
Fully heat-treated " Y " alloy ..	96 lb.	5 mins.
Fully heat-treated D.T.D. 324 ..	96 lb.	5 mins.
Tin-plated surface	96 lb.	10 mins.
Lead-plated surface	96 lb.	15 mins.
Anodized oil impregnated "Y" alloy	96 lb.	120 mins.

Bearing properties.— Results of a series of tests on the friction of various cast and wrought alloys over the working temperature range of a piston,[7] show that the forged alloys exert proportionately lower friction all over the temperature range than the cast alloys.

The preceding table shows the effects of different surface treatments on the bearing properties under oil shortage conditions.

7 Hiduminium Data Sheets.

Ring-groove wear is difficult to tie down to any given property. While we believe that an alloy with a high hardness at the operating temperature is better, the fact remains that the aluminium-silicon alloys show better wear resistance than the Al-Cu-Ni-Mg type and this must be due to the presence of a large number of hard silicon particles in the matrix. In addition, there is some reason to believe that the R. A. E. alloys show very good resistance to ring-groove wear, but the alloy which is generally considered best of all is the KS. 280 type containing approximately 20% silicon. The micro structure of this alloy is shown in Fig. 27, it has a very high proportion of hard particles of silicon and has been found very resistant to abrasion.

Under extremely bad conditions of lubrication and abrasion it has been found that service equal to that obtainable with a cast-iron piston, with only a small sacrifice in weight, may be obtained by the use of a "ring carrier" insert[8] and of austenitic cast iron which has a coefficient of thermal expansion slightly less than that of the aluminium piston alloys.

The insert is placed in the mould prior to casting and the differential contraction of the two materials holds it firmly. Fig. 28 shows a London 'bus piston after 90,000 miles service. The two top rings situated in the insert functioned satisfactorily long after the lower ring situated in the aluminium had disintegrated and demolished the grooves. Such pistons have given satisfactory service for over a quarter of a million miles.

Acknowledgments

The authors wish to thank Messrs Specialloid Ltd. for permission to publish this paper and to record their appreciation of the assistance given them by their colleagues—Mr. O. S. Plail for his assistance with the illustrations and Mr. H. Dorner for his advice on bearing properties.

8 British Patents, Nos. 483,993, 557,070, and 581,527.

Aluminium and Its Alloys

Contd. from page 186

engines, etc., are being increasingly made in suitable alloys.

The use of aluminium materials for moving parts and portable equipment has increased considerably. In the textile industry, for instance, aluminium is proving advantageous for many fast moving parts and beams up to 4 ft. in length are now in use. For portable tools too, aluminium applications are developing rapidly. In both these fields the use of aluminium has widened considerably, due probably to the increased experience of this material as a result of the war effort. In the chemical processes industries too, the construction of equipment in aluminium and aluminium alloys has made considerable headway; such equipment as storage tanks, stills, heating coils, stirrers, vats, receptacles, kettles, condensers, retorts and crystallisers are made and some of the products handled by aluminium equipment include foods, fruit juices, sugar, candy, milk, nitric acid, certain organic materials, soap, rubber and varnish. Steam-jacketed aluminium kettles are used for cooking in canning factories, and much aluminium is used for dairy equipment.

No attempt has been made to detail applications in the electrical and several other important industries, but sufficient has been said to indicate that not only is aluminium successfully contributing to span the transitional period from war- to peace-time activities, but the industry is establishing its position in competition with other materials, and the future will see developments not less important than those so far achieved. There is no doubt that the need for aluminium and the extent of its application will continue to increase and, while the production of primary aluminium will continue to be a major consideration to provide supplies, it is important that secondary aluminium is now produced in such reliable compositions, in conformity with national specifications, that its use as a general purpose material has greatly assisted application development.

Although it is true that some of the present applications of aluminium and its alloys can be regarded as of a temporary character to span a transitional period, the reasons for the great development of the aluminium industry should not be overlooked. They are to be found largely in the inherent properties of the metal itself and its ready adaptability to industrial requirements. Yet, it will be appreciated, each incursion into new fields of industrial application is preceded by much circumspection and careful analyses of the problems to be encountered, and many exhaustive tests to determine the precise aluminium alloy most suited to the work in hand. To-day, there are few, if any, industries in which aluminium and its alloys, in one way or another, do not play their part.

The Influence of Chemical Composition and Quality of Raw Materials on the Physical Properties of Silumin Gamma

By Vlad. Zednik, Ing. Dr.

For casting purposes, an aluminium-base alloy with additions of Si and Mg proved to be one of the best from the point of view of good all-round properties. This alloy, known commercially as silumin (Aipax) gamma, is the result of research in alloys of the aluminium-silicon type. It derives its properties from the binary Al-Si eutectic alloy modified, according to the Pacz patent, with sodium. The development of these alloys is interesting in two ways: first, the tendency to furnish cheaper raw materials for the production of the alloy, and second, the simultaneous improvement of the physical properties of the finished castings. The reciprocal influence of both these efforts and the analysis of results and experiences gained in the foundry of Skoda-works are the content of this paper.

Raw Silumin Production Methods

THE production of raw silumins is based on three possible methods :—

1. By alloying pure aluminium with pure silicon.
2. By electrolysis, the electrolyte being that used for the production of aluminium, with additions of Si or an Al-Si temper alloy.
3. By alloying pure aluminium with a temper alloy containing a high percentage of Si. The temper alloy is made by reduction of kaolin and silica with carbon.

The first method is the most expensive, and for this reason it is of limited practical application. The third method is the cheapest, and is extensively used for the production of silumins, especially in Germany. The direct electrolytic method required great experience and is more costly than the German method. Cheap electricity, however, can balance out the production costs. Hence, countries like Norway and France could apply this method and bring it to a high degree of perfection.

However, the usual impurity content depends in all cases on the preliminary treatment of raw materials used for the production of silumins. Furthermore, with the German method, carbides, phosphides and oxides are increased, due to the method of production of the temper alloy. Bricks made from a mixture of Al_2O_3, kaolin and silica are reduced by carbon in an electric arc furnace. The bottom electrode of this furnace is fixed, while the mobile electrode is suspended from the roof of the furnace. The temper alloy made in this way contains a certain amount of Ti and Ca, so that the content of the undesirable elements Ti and Ca in the synthetic silumins is usually higher than in silumins made by direct electrolysis. The influence of these impurities on the quality of raw materials and the finished products will be discussed later.

Development of Al-Si Alloys for Castings

The mechanical properties of silumin and their excellent castability compete successfully with previous Al-Cu, Al-Zn and Al-Cu-Zn alloys. The only difficulty which arose at the beginning of the development of silumins was in attaining a sufficiently low iron content. The higher the iron content the greater are the amount of Al_4Si_2Fe needles formed, which destroy the useful properties of the alloy. The complex needle-like crystals which, besides Fe, contain a certain amount of Ti, are formed at iron percentages as low as 0·6% of Fe, and this figure is accepted as the highest possible iron percentage for high-grade silumins.[1]

It was found later that the detrimental influence of Fe and Ti could be minimised by small additions of Mn and or Co. In such cases more favourably-shaped crystals of Fe-Mn-Al-Si and Fe-Co-Al-Si, respectively, are formed. Their constitution has not yet been ascertained accurately. In common silumins (the binary aluminium-silicon alloys) Mn has been used to compensate for the iron content principally because of its cheapness. The nature and the conditions of the compensation of iron by Mn has not as yet been sufficiently studied.

Low hardness, about 50–60 BHN, with a low yield point of about 8 kg./mm.^{2} and a moderate tensile strength of 18 kg./mm.^{2}, were the main objections of these alloys for engineering applications. The properties could only be very slightly improved by heat-treatment even though the solubility of Si varies considerably with temperature, varying from 0·1% Si at room temperature to 1·6% Si at the eutectic temperature. The Junkers Co. tried to improve the physical properties by the addition of 0·8% of Cu, causing thereby the precipitation of Al_2Cu from the solid solution, but even this alloy did not lend itself to heat-treatment. The yield point reached was only 10 kg./mm.^{2} with tensile strength of 20 kg./mm.^{2}, 2–5% elongation and 60–70 BHN. Hence, the copper additions did not stimulate the technological development of silumin.

A new field in the development of silumins was opened with the addition of Mg, resulting in the alloy designated silumin gamma. It threw new light on the advantages and disadvantages of various methods of production of raw materials, on the compensating power of Mn and Co, and on the interesting influence of impurities and the structure of raw material on the quality of products and the reliability of production, which played an important part in the aircraft industry and its wartime potential.

The original silumin gamma was of about eutectic composition, containing between 12–13% Si in the "modified" state, and 0·3–0·5% Mg. In view of experiences with the original silumin alloys, the eutectic Si-content was selected in order to ensure optimum

1 The ternary Al-Fe-Si eutectic contains 0·5% Fe (Fuss). Sachs values (Praktische Metallkunde, Springer, 1933), 0·8–1·0% are too high and contradict theory as well as practical experience.

castability, while the presence of sufficient Mg, in the combined Mg_2Si form, was intended to ensure good response to heat-treatment. The solubility of Mg_2Si varies from about 2% at the quasibinary eutectic temperature, 595° C., to about 0·5% at 30° C., provided Si and Mg are not in excess. According to Hanson and Gayler the solubility is lowered by an excess of Mg. Assuming Si and Mg not in excess, percentages higher than 0·3% Mg were recommended by Silumingesellschaft in Central Europe as the apparently optimum

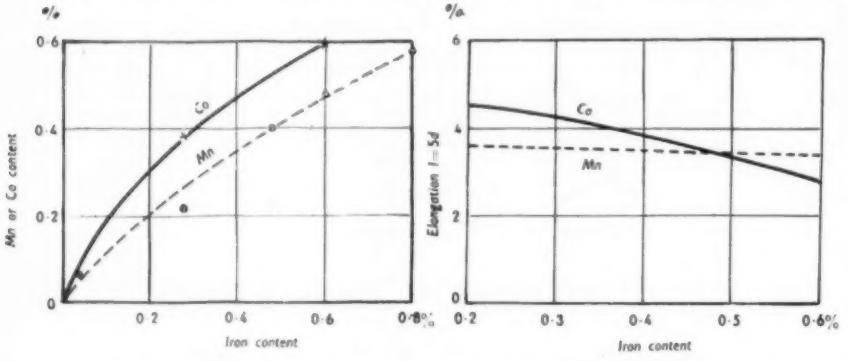


Fig. 1. Fig. 2.

Fig. 1.—The relation of manganese or cobalt respectively, to varying iron contents according to Gurtler. Fig. 2.—The influence of the iron content in silumin on elongation when compensated with manganese or cobalt, respectively, according to Gurtler.

Mg content. These percentages correspond to and are above the maximum solid solubility of Mg_2Si at normal temperatures.

Figures quoted in the German literature, showed that the Mg contents, depending on the composition of raw materials produced by the company mentioned, varied in the mass production of aircraft castings in 1939 between 0·37–0·55% Mg.

In the patent application covering silumin gamma, Mn and similar metals, as for instance, Co, are mentioned as iron compensators, in addition to the recommended Mg contents. German scientists tried to prove that Mn was more efficient than Co as a compensator of higher Fe contents, especially as the sources of Co became inaccessible during the war.[2]

Gürtler, in the chapter of the Jahrbuch, 1941, der deutschen Luftfahrtforschung, dealing with the development work on silumin gamma, gives the amounts of Mn or Co required to suppress the harmful effect of iron, in alloys with varying iron content, as shown in Fig. 1. The influence of the optimum Mn or Co content on the elongation, for varying percentages of iron, is given in Fig. 2. This author's numerical data, however, point to the desirability of using Co instead of Mn. According to him, the complex crystals form ternary eutectics at 0·3% Mn and 0·6% Co, respectively. Hence, the formation of iron-rich primary crystals occurs relatively much sooner in alloys with Mn than in alloys with Co as compensator. Furthermore, when Mn is used, there is a tendency towards segregation to which reference will be made later.

It may seem that the casting properties of silumins at this stage of development should compare with those of eutectic cast iron, while the treatability should be comparable to that of steel. It is important to remember, however, that the mode of deposition of Si in silumin differs from the mode of separation of graphite in cast iron. Further, the process of saturation of the solid solution and the volume changes caused by the dissolution of Mg_2Si in Al differ from those caused by cementite in steel.

Moreover, the fact that the Si content of the alloys corresponded with the binary eutectic, made modification by Na more difficult. Also, the tendency of aluminium-base alloys towards under-cooling, which causes the production of the alpha phase even in the eutectic alloy, made the quasiprimary separation

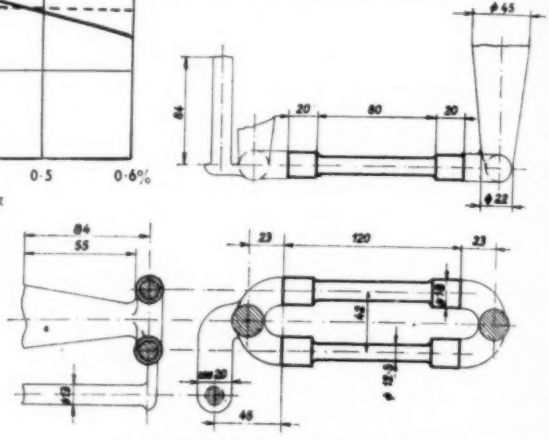


Fig. 3.—Design of separately cast test bars.

of coarse Si likely to occur with slower cooling. For these reasons a slightly hypoeutectic alloy proved to be of better value for complicated casting in the aircraft industry, the effect of this change was not found to be detrimental to the mechanical properties, since the increased amount of the separated alpha phase has only a slight influence on hardness and, indeed, has a beneficial effect on the tensile properties.

Experiences Gained in Skoda Works During Mass Production of Silumin Gamma Castings

The effects of the Mg content and of the varying amounts of Mn and Co are evident from the comparative tests and production statistics compiled during the mass production of castings in Skoda Works, Plzen, Czechoslovakia. In this works silumin castings have been made for the last 20 years.

Before the war, French raw materials mostly were used for these castings. During the war, the Skoda Works as was general in Central Europe, depended on inferior German raw materials. The production of high-quality silumin castings, therefore, terminated, for all practical purposes, on the outbreak of hostilities. But, even though the quality of the product deteriorated rapidly during the war, valuable experience has been gained, and it has been supplemented by the official interchange of experiences with German foundries.

The Skoda Works, which comprises metallurgical plants, general engineering, motor works and ammunition factories, benefited considerably from the close

2 G. Sachs, Practische Metallkunde, Springer, 1933, p. 95–97; V. Fuss, Metallographie des Aluminiums und seiner Legierungen, Springer, 1934, p. 108; DRPA 40988/40b.

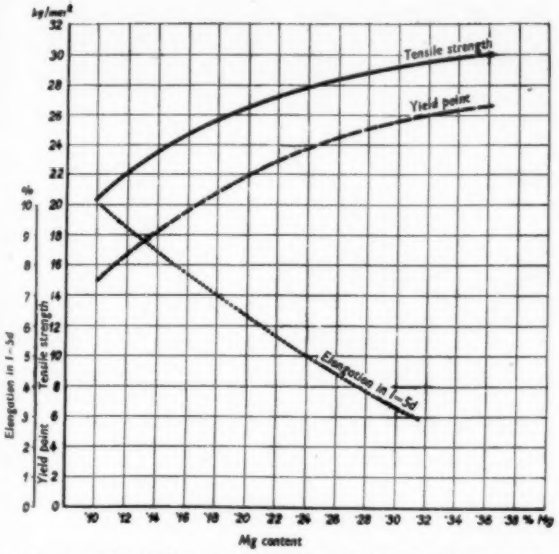


Fig. 4.—Mechanical properties of separately cast test bars of silumin gamma made from French alpaxes in relation to magnesium content.

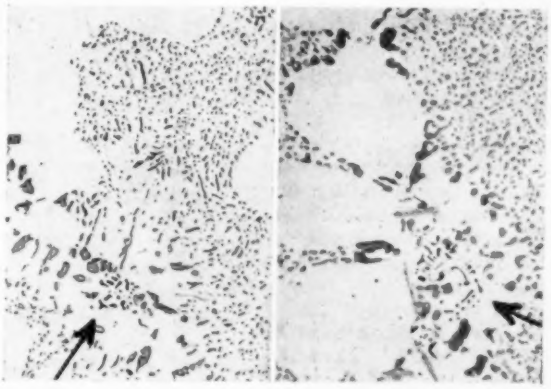
relations developed between designing engineers and metallurgists. From the early days of the development of light alloys, metallurgists had to produce materials satisfying the engineering requirements and needs. Consequently the importance of the yield point, fatigue limit, notch sensitivity, damping capacity, elongation, and toughness predominated over the static tensile strength. That is why technological research on silumins was preferred to that on other light alloys with low yield point. Special attention was also paid to methods of testing.

For the purpose of research, control, and statistics, test bars have been cast in green sand as shown in Fig. 3, in addition to standard test castings used for estimating the gas content and studying structural homogeneity. The simplicity of the test bars makes it possible to preserve indentical casting conditions, and, from the results obtained, to judge the quality of individual melts, or the quality of the raw materials used for production. On the other hand, cast-on test bars indicate, to a certain extent, the quality of the finished casting. They are, however, specifically influenced by the shape of the casting and their position on the casting. The Na content and the amount of segregation in the cast-on test bars are both influenced by the usually long contact of the metal with the mould, of which the moisture content and reactivity depend partly on the atmospheric conditions. For these reasons the author considers the results of tests on separately cast bars to be more indicative of the physical properties of various types of silumins and of individual melts in mass production. Only if the castings are of identical shape, the test bars taken in the same place on the casting, and the moulding and pouring technique remain unchanged during production, can the results on the cast-on test bars be considered reliable.

In comparing the statistical results of the development research and of the mass production of silumin castings, consideration will be given primarily to the type of raw materials, the Mg content, and to the mode of compensation of iron content. The amount of the other elements fluctuated only slightly and did not, in general, cause much variation in the mechanical properties, an exception must be made, however, of impurities like Ca[3], carbides[4], phosphides[5]; the amounts present are principally governed by the method of production of the raw materials and their determination in the foundry laboratories proved difficult.

All other detrimental effects, such as those caused by bad quality of moulds or unusual composition of the alloy, are excluded from the statistical consideration, as such castings had been rejected before the heat-treatment.

The effect of Mg content on the mechanical properties of silumin gamma made from French alpaxes and containing 0·4–0·5% Co and 0·35–0·4% Fe, is illustrated in Fig. 4. This figure gives the results of the determination of mechanical properties made on test melts in 1934. At that time, when the dominating Company, Silumin Gesellschaft guaranteed a tensile strength of 20–30 kg./mm.², and an elongation of 0·5% in a sand-cast alloy containing 0·3–0·5% Mg, and when the aircraft factories required a minimum tensile strength of 20–22 kg./mm.² with a minimum elongation of 2%, this discovery, illustrated in Fig. 4 was rather surprising. It led to a fundamental decrease in the Mg content, to 0·16–0·22% Mg.[6] Though the hardness of the alloy dropped from about 90 BHN min. to 75 BHN min., the workability of the alloy, after some adaption of the angles of the cutting tools, proved to be good. This proved that even alloys containing lower percentages of Mg are capable of adequate age hardening for the purpose required. Further, the castings became more homogeneous, as in thicker sections Mg_2Si is formed at percentages slightly lower than 0·3% Mg. It does not dissolve completely during the heat-treatment, as can be seen in Fig. 5, which shows the formation of Mg_2Si at 0·24% Mg under conditions of slow cooling. But the primary formation of Mg_2Si is detrimental even when the whole of the precipitate goes into



(a) 0·24 Mg, 9·36 Si, 0·42 Fe, 0·41 Mn, 0·10 Ti, 0·008 Na. x 150.

(b) 0·26 Mg, 9·18 Si, 0·46 Fe, 0·42 Mn, 0·11 Ti, 0·005 Na. × 150.

Fig. 5.—The segregation of Mg_2Si in cast-on test bars (11 mm. thick).

3 After adding 0·05% Ca silumin had to be scrapped as not fit for use.
4 According to Czochralski the solubility of Al_4C_3 in alpha-Al is 0·05%.
5 According to German applications for granting patents (1944/45) it is desirable to keep P content in the silumin below 0·0002%.
6 The Mg-content has been found in all cases by the spectroanalytical method.

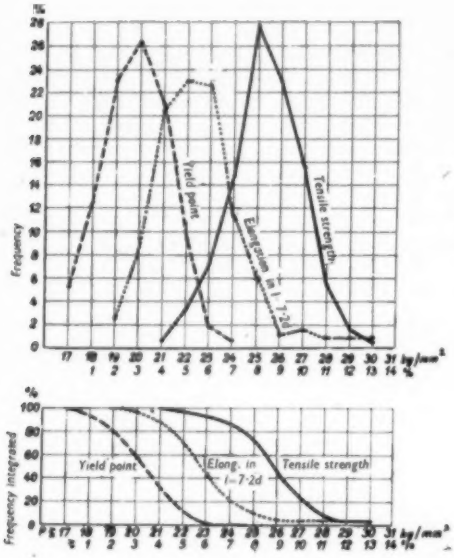


Fig. 6.—Frequency curves of mechanical properties of separately cast test bars in the mass production of silumin gamma alloyed with cobalt and made from French raw materials.

solution during the heat-treatment ; due to volume changes, microcavities are formed which cause deterioration in the mechanical properties of the alloy.

The frequency curves and their integrals in Fig. 6 give the results of mechanical tests on separately cast bars during the mass production of silumin gamma containing Co and made from French raw materials supplied by Aluminium Francaise, 1934–37. The arithmetical means of several thousand results are as follows :

Average yield point 20·5 kg./mm.²
Average tensile strength 25·2 kg./mm.²
Average elongation (l = 7·2d) 5·5%

Statistical examination of results from test bars cast-on the parts of aircraft motors of the Hispano Suiza type LM 701, taken on delivery, showed the mechanical values given. The improvement in the methods of production is obvious from the results of tests on testpieces cast on the motor casings, cylinder blocks and other castings,

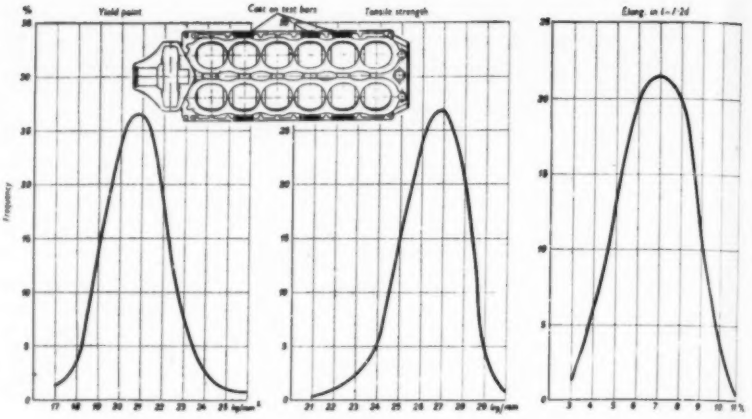


Fig. 8.—Frequency curves of delivery tests on test-bars cast-on to crankshaft casings of silumin gamma, made from French raw materials, and alloyed with cobalt.

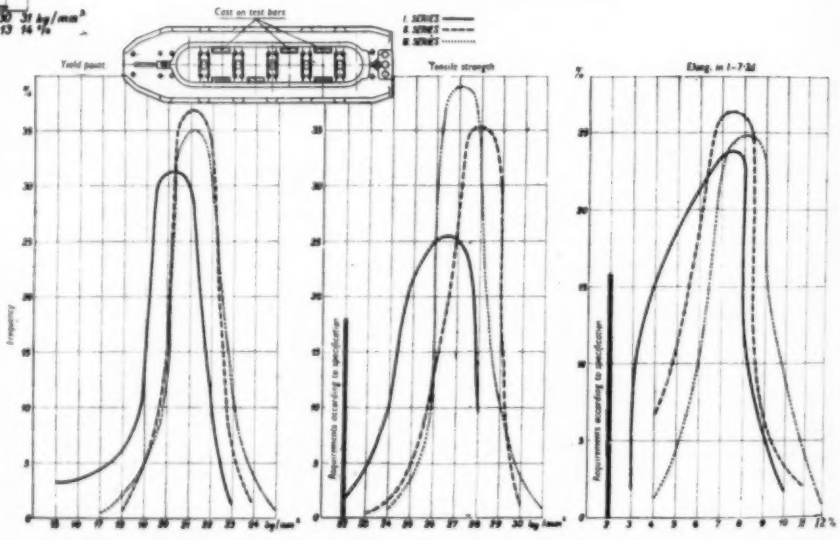


Fig. 7.—Frequency curves of delivery tests on test-bars cast-on the base of motor casings from silumin gamma, made from French raw materials, and alloyed with cobalt.

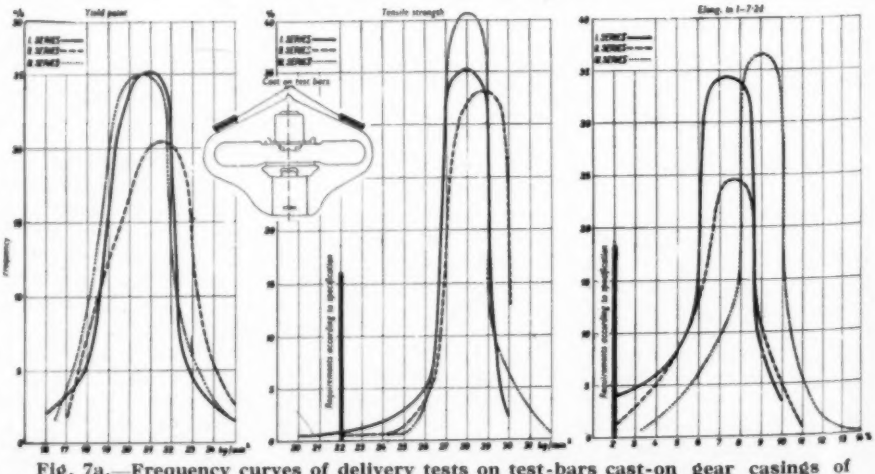


Fig. 7a.—Frequency curves of delivery tests on test-bars cast-on gear casings of silumin gamma, made from French raw materials, and alloyed with cobalt.

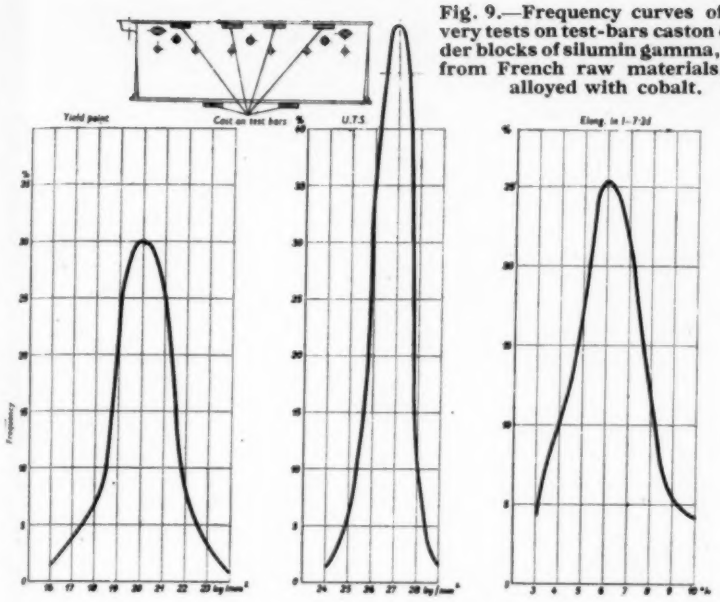


Fig. 9.—Frequency curves of delivery tests on test-bars caston cylinder blocks of silumin gamma, made from French raw materials, and alloyed with cobalt.

	Mark	U.T.S. kg/mm²	Elongation l = 5d %	B.H.N. 15/500/30
Cast on test bars ..		27·6	6·7	86
Bars cut out from the casting	C1	28·0	7·3	88
	C2	28·0	7·5	93
	C3	28·1	8·3	87
	C4	28·4	7·7	93
	C5	27·4	7·5	85
	C6	27·4	5·8	89
	C7	27·4	7·6	86
	C8	27·6	7·9	93
	C9	27·8	3·0	85
	C10	25·4	2·9	85
	D11	27·7	9·0	86
	D12	28·2	9·6	85
	E1	26·5	4·5	93
	E2	27·2	7·2	85
	E3	27·0	5·4	85
	E4	27·6	6·5	94
	E5	27·1	7·5	80
	E6	28·0	6·3	95
	E7	28·2	9·5	85
	E8	28·3	10·3	86
	E9	25·5	2·5	88
	E9	26·8	3·5	90
	E10	26·7	4·0	89
	E10	24·6	2·1	87
	F11	27·5	8·4	84
	F12	28·9	8·0	86
	G1	28·0	8·0	85
	G2	26·8	5·1	83
	G3	27·9	7·4	95
	G4	28·0	6·3	88
	G5	27·5	7·7	90
	G6	27·6	5·4	89
	G7	27·1	7·5	90
	G8	28·3	9·1	93
	G9	25·6	2·8	95
	G9	27·2	3·6	85
	G10	25·6	2·3	95
	G10	25·8	2·5	85
Average		27·3	6·3	88

taken separately for each production series as shown in Figs. 7, 7a, 8 and 9. The curves show the uniform quality of material and the reliability of its production. It is necessary to remark that the process of modification by sodium has been modified within the framework of the Pacz patent so as to attain a distribution of sodium as uniform, and as favourable, as possible for each kind of casting. It was demonstrated that an excessive Na content can be as detrimental to the casting as an insufficient one. When silumin was produced from French raw materials it was possible to obtain a uniform Na content throughout by treating the melts with a mixture of NaCl and NaF, with additions of KCl in proportions corresponding to the refining temperature desired. To attain a uniform Na content when refining with metallic sodium is not an easy matter, due to the wide difference in the specific gravities of Na and Al. The excess of Na in silumin gives rise to porosity and

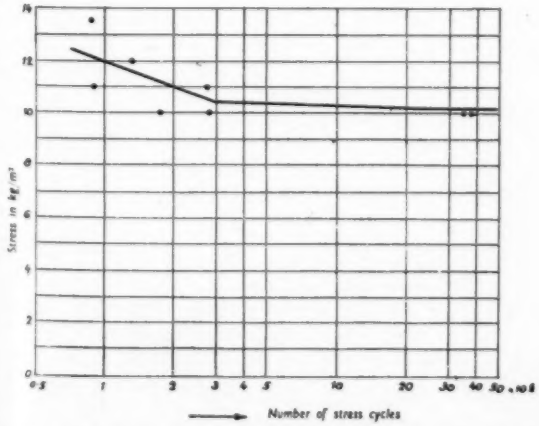


Fig. 11.—Fatigue limit in bending bars cut from Skoda casting illustrated in Fig. 10. Bars are marked A 1–A 8 in Fig. 10.

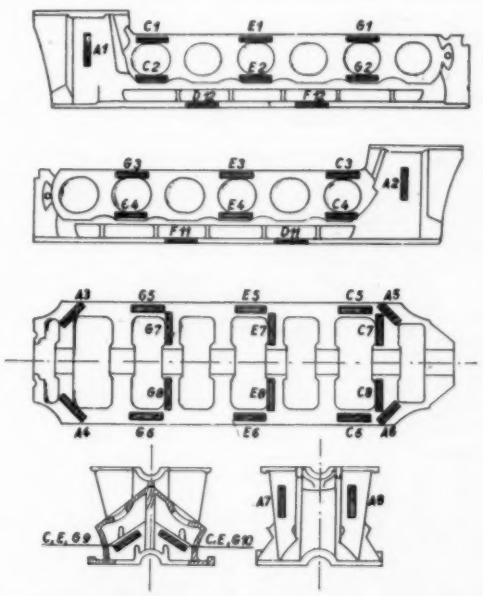


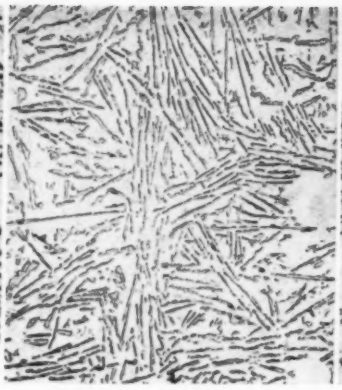
Fig. 10.—Test results of bars cut from a Skoda casting of silumin gamma, made from French raw materials, and alloyed with cobalt.

oxide envelopes, as it raises its affinity for H_2O and O_2, causing hydrogen porosity and oxidation of Na and Al.

It is interesting to note that even after the occupation of Czechoslovakia, when the German military authorities handed over captured aircraft motors to a specialised firm in the Reich, the German specialists were not concerned with the yield point, as can be seen from Fig. 10, which is a typical example of a German test

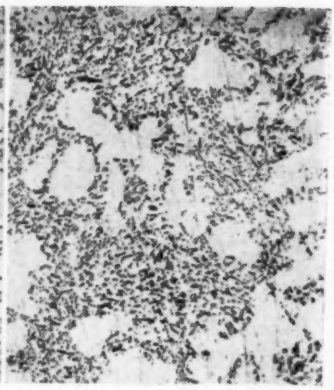
Composition : 0·18 Mg, 9·03 Si, 0·57 Co, 0·02 Mn, 0·39 Fe.

Fig. 12.—Microstructure of a sample cut from the thickest wall of the casting illustrated in Fig. 10.



Composition : 0 Mg, 10·5 Si, 0·32 Fe, 0·02 Mn, 0 Co, 0·02 Cu, 0 Na.

Fig. 13.—Raw alpax made by L' Aluminium Francaise. Microstructure taken at middle of the pig.



Composition : Trace Mg, 9·5 Si, 0·35 Fe, 0·03 Mn, 0 Co, 0·02 Cu, 0·002 Na.

Fig. 14.—Raw alpax made by Aluminium Union. Microstructure taken at middle of the pig.

report showing the location of the test bars and the individual results. The fatigue limit of silumin gamma made from French raw materials and alloyed with Co, taken on test pieces of the same casting, is given in Fig. 11. The structure in the thicker section G_2 is shown in Fig. 12. Due to the negligible colour difference, the finely distributed Si in the eutectic and the complex Fe-Co-Si-Al phase are not easily distinguished from each other in the reproduction.

From these results the high quality of silumin gamma made from French alpax and containing Co is evident. When, due to the political situation, raw materials had

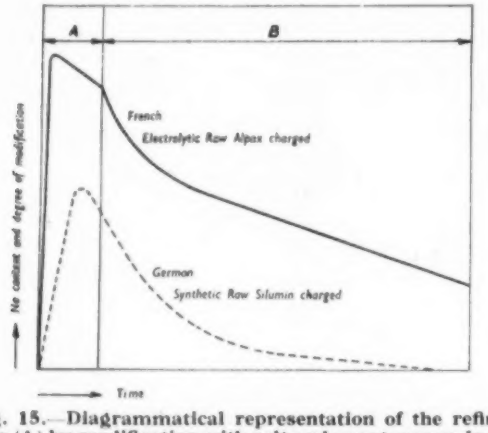


Fig. 15.—Diagrammatical representation of the refining rate (A) by modification with salt and spontaneous drooping of the modified (refined) state (B) after the salt has been removed.

to be bought in other countries and tests were made with silumin gamma from Swiss and Canadian alpaxes, it was surprising to find, with raw material and finished products of identical composition, and with identical methods of production, that the values of the mechanical properties were fundamentally lower. At the same time the structure was less homogeneous, and the quality suffered through inferior castability and the tendency to variable shrinkage.[7] With tensile strengths of about 25 kg./mm.^{2}, elongations reached only 2–3% as compared with 7% with silumins made from French alpaxes.

Comparative experiments revealed that the cause of the deterioration had to be sought in the raw material only, which, apart from the higher impurity content differed from the French raw material mainly in the structure. In the Swiss and Canadian raw materials the Si existed in a more or less modified eutectic form. Hence, the recommendations of the delivering firm, based mainly on the silky fracture of pigs made more effective by the refining action of sodium, could not compensate for the inferior quality of the raw material. French alpax, Fig. 13, showed a coarse grain and unrefined eutectic structure compared to that shown in Fig. 14.

In view of the need to use greater quantities of modifying salts to ensure sufficient refining effect, the conclusion was reached that some elements present in the raw material were exerting a deleterious effect. Melts showed a tendency to lose their modification, hence, their structure was never completely homogeneous. This was found metallographically from the fineness of the Al-Si eutectic, and from variations in the Na content as determined by a modified Scheuer[8] analytical method on samples taken from the bath at certain intervals after the refining salt has been skimmed. The results of numerous experiments are shown schematically in Fig. 15.

7 Most of the cases concerns eutectic separation.

8 *Metallkunde*, 1933, p. 133 and following.

To be continued

The Specification of Meehanite Metal

By an inexplicable error the review of a booklet recently issued by the International Meehanite Metal Co., Ltd., given on page 163 of the January issue of this journal, appeared under the heading, "The Specification of Meehanite Steel." As many readers will know, Meehanite metal is cast iron, but there are several types, each developed to cover a field of service for which it is best suited. Meehanite iron castings are produced by controlled processes and the new booklet provides the designer and engineer with background information, as well as reliable data, to assist in making the best use of the type of Meehanite metal for a specific casting, whether for general engineering, or heat-, wear-, or corrosion-resisting purposes.

Die Casting Progress

Part III—Aluminium Alloy Die Casting

By Dr. A. C. Street

Developments in the production of aluminium die castings are reviewed. Reference is made to both gravity and pressure die casting. In this country greater progress has been made in the theory and practice of gravity die casting of aluminium alloys, which is reflected in improved die design and manipulation and in general production technique.

ALTHOUGH many millions of aluminium alloy pressure die castings are produced each year in this country, it is certain that in quantity, and even more in bulk, the majority of our light alloy die castings are produced by the gravity process. Remarkably ambitious gravity die castings are being made for the automobile and aircraft industries and to anyone who thinks of this process as a sort of poor relation to pressure die casting it would come as a surprise to discover the technical control that is needed to make possible such gravity castings as for example the automobile cylinder head, illustrated on Fig. 1.

In recent years similar enterprise has been shown in the manufacture of aluminium alloy gravity die castings used in housing. For example, the well made aluminium alloy die-cast rain-water fittings, which are on the market, have merits which make their use advantageous, quite apart from their welcome availability. Many prefabricated and other houses contain the gravity die-cast aluminium alloy sink. This is not a perfect job from a housewife's point of view and those which the writer has seen in use have a dull colour which is not altogether attractive ; also there seems some tendency to contain pinholes, which detract from the surface appearance. Nevertheless, the achievement of producing such a large gravity die casting in bulk has been a considerable one. Another interesting development of aluminium gravity die castings in the home is the manufacture of furniture, in which the gravity process has been used and chairs of attractive design produced.

The writer considers that the technique of gravity die casting of aluminium alloys has been mastered to a greater extent than any other branch of the industry. In pressure die casting, for example, the study of what takes place when metal enters and fills the die is still incomplete. In the gravity casting of aluminium alloys, however, striking progress has been made in the theoretical side of die casting and the knowledge gained is reflected in improved die design and manipulation. The rate of cooling of the metal in the mould, for example, is an important factor in the making of large components. To control rate of solidification certain parts of dies are gas heated, or given refractory dressings. Furthermore, the gravity process has become more and more mechanised, it is not uncommon to find each die caster " working to the clock," so that, for example, the time between pouring and die opening is controlled ; in some cases this has been carried further and light signals given to the operator for each stage in the process.

In spite of the undoubted progress made by gravity die casting one feels that the possibilities of pressure die casting have been explored only tentatively and that the coming years may show pressure die-casting achievements just as spectacular as those of the " gravity "

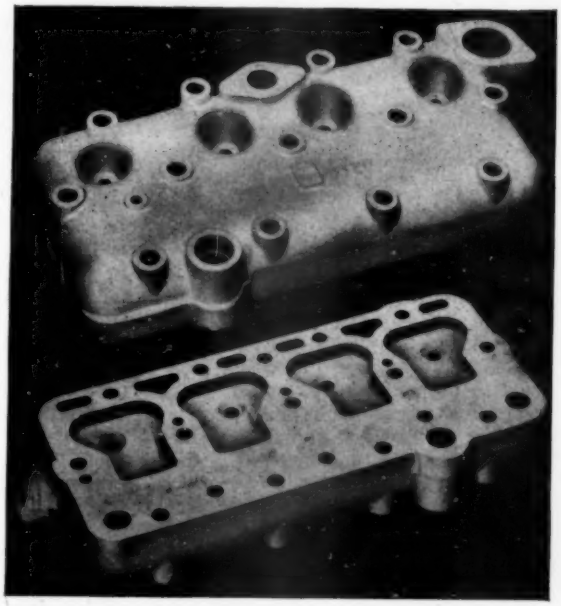


Fig. 1.—A gravity die cast four cylinder engine cylinder head, showing top and underside views. A sand core is used for the water jacket.

section of the industry. It takes a long while to develop and build huge die-casting machines capable of producing aluminium alloy die castings weighing 10 lb. or more, but from the point of view of surface appearance and accuracy the widening use of the pressure process seems only logical. For example, the writer calls to mind the three-legged base of an office chair which is now being made as a pressure die casting and though he is not aware that the pressure process has been used for making domestic furniture, the office chair pressure casting seems to indicate that other types of furniture will be attempted in the coming years.

In considering pressure die casting it should be remembered that there are two main types of machine in wide use. The hot chamber machine includes a molten metal container and " gooseneck " in the structure of the machine ; the plunger is, therefore, in continual contact with molten metal. In cold-chamber plant the alloy is melted in a separate crucible near the die-casting machine. For each " shot " the operator ladles metal from the crucible into the cylinder of the machine ; he then operates the plunger which injects the metal into the die cavity.

Hot-chamber machines are faster in operation than

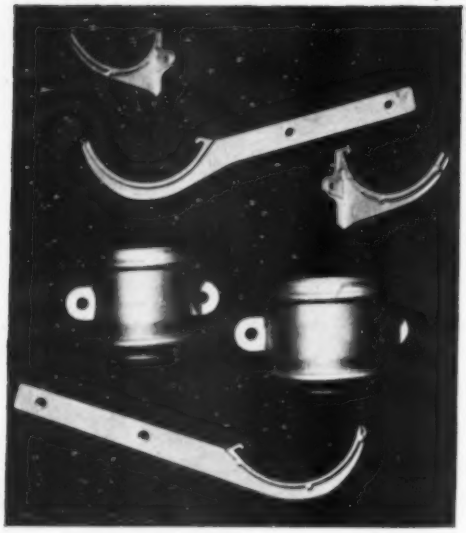


Fig. 2.—Rain water fittings die cast in D.T.D. 424. The brackets are pressure cast and the remainder gravity cast.

cold-chamber ones and they have some technical advantages in, for example, the making of zinc alloy die castings which are to be electro plated. The fact that the plunger is in contact with the molten metal is a disadvantage for working at elevated temperatures and cold-chamber machines are, therefore, preferred in the pressure die casting of aluminium alloys. The cold-chamber machine works at higher pressure than hot-chamber ones and in aluminium alloy die casting this higher pressure yields more solid die castings.

Up till about 1943 there were only a comparatively few pressure die casters who specialised in light-alloy production. The remainder, using hot-chamber machines, concentrated largely on the zinc alloys. At about that time a sudden drop came in the consumption of zinc alloys for armaments (due to the fact that the industry had produced what was considered to be a sufficiency of zinc alloy components for the country's munition requirements). This led to an extension of the use of aluminium alloy pressure die castings, and many concerns installed cold-chamber machines to cope with this production. Then in the following years the price of zinc alloy rose so that now in many cases an aluminium alloy pressure casting costs less than one in zinc alloy. This again has caused pressure die casters to produce an increasing proportion in aluminium alloy.

The dimensional accuracy of aluminium pressure die castings is of the order of plus or minus 0·0025 in.

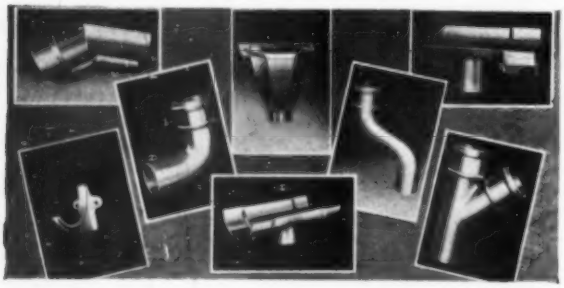


Fig. 3.—Gravity and pressure die castings in D.T.D. 424 for rain-water water fittings.

Fig. 4.—Pressure die casting of vacuum cleaner body, showing undercut recess.

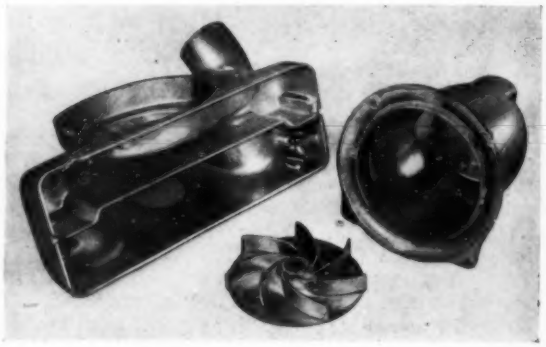


Fig. 5.—Aluminium silicon alloy pressure die castings for vacuum cleaners.

per in. Section thickness usually lies between $\frac{9}{64}$ in. and $\frac{5}{32}$ in. In this connection it must be added that one of the factors limiting the use of pressure castings is that change of section from thick to thin is less readily accomplished than in gravity die casting. Tapers of about 0·01 in. per in. are usually needed. External threads can be cast, up to 24 threads per in., but usually are not to be recommended; it often proves cheaper to machine threads. Undercut designs can be accomplished in pressure die castings, as is shown in the illustration of a vacuum cleaner body Fig. 4. As in any die-casting process the inclusion of an undercut slows production; generally pressure die castings include undercuts less often than gravity castings. The use of sand cores in pressure casting is impracticable.

The comparatively high melting point of the die-cast aluminium alloys means that pressure dies should be heat-treated before use. Die lives of about 50,000 shots are customary for aluminium pressure die castings of fairly complicated design. Particularly when the parts are small much longer die lives are obtained; for example one die for aluminium stove burners is reported from America to have produced one and three quarter million castings from the same four-impression mould.

Cold-chamber die-casting machines are almost exclusively used for aluminium, about 2–4 tons/sq. in. being commonly applied, but up to 15 tons/sq. in. being used

on occasion. So far, aluminium pressure die castings have been much more widely used for domestic appliances and electrical gear than for automobiles. Vacuum cleaners are largely built around pressure die castings and washing-machine manufacturers use them in large amount. From America it is reported that the use of aluminium alloy pressure castings, for a typewriter body eliminated nine machining processes, saved weight and finishing operations. The writer was impressed with the design of the Swiss " Bernina " portable sewing machine which has been beautifully re-designed for die casting, and the American book, " Die Castings for Engineers " shows a model from the U.S.A. which embodies six aluminium alloy die castings. In the mass production of fractional horse-power motors, aluminium alloy pressure castings are widely used.

The major part of aluminium pressure casting production has so far been in 2L33, the well-known alloy with about 12% silicon. This possesses greater fluidity than any other aluminium casting alloy, so that thin sections and intricate detail can be produced. The alloy as used in pressure die casting is not " modified " by sodium additions, but it is interesting that in its pressure-cast form the microstructure is similar to that representative of modified aluminium silicon alloy, because of the rapid cooling which takes place in pressure casting. The corrosion resistance of this alloy makes it suitable for use in marine work, food and chemical plant.

Fig. 6.—Pressure die-cast binocular bodies in aluminium-silicon alloy.

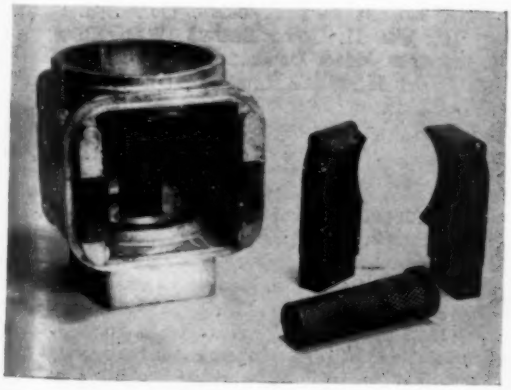


Fig. 7.—Die-cast magnet body incorporating inserts.

Fig. 9.—Gravity die-cast heavy duty commercial vehicle brake shoe, and a small gear casing.

The aluminium-copper-silicon alloy D.T.D. 424 (silicon 3–6%, copper 2–4%) was developed as a means of making controlled use of the large quantities of scrap aluminium alloy, from damaged aircraft, a development in which the late Mr. Percy Pritchard played a leading part. This alloy was not very well received by founders at first since they were accustomed to the easy working of L33, but when experience had been gained in its use it was readily accepted. Even now the use of D.T.D. 424 in pressure die casting is somewhat limited ; the tendency to hot cracking causes trouble occasionally and in any case taper and draft have to be greater than is required for the straight aluminium-silicon alloy. The greater ease of machining, however, is an advantage which causes D.T.D. 424 and some other aluminium-copper-silicon compositions to be preferred in many cases.

LAC 112A, with 9–11·5% silicon, 0·75–2·5% copper and small quantities of other elements, is often used where the extra expense of L33 is not fully justified; this alloy is somewhat easier to machine than L33 and its resistance to corrosion by ordinary atmospheric conditions is nearly as good. In the U.S.A. an alloy with 9% silicon and 3·5% copper was developed in about 1943 and standardised for pressure castings required in ordnance work.

Fig. 8.—Gravity die-cast main body pillar for saloon car.

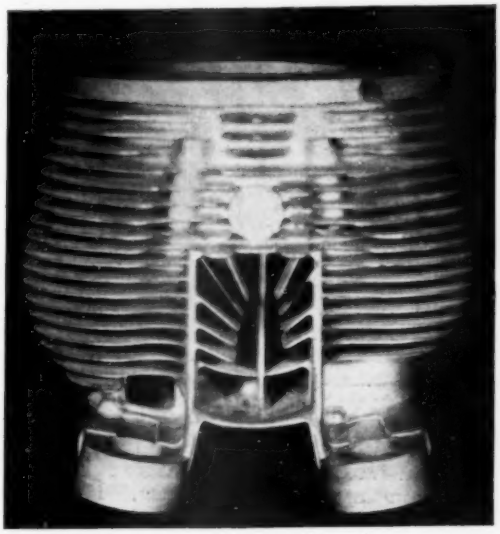


Fig. 10.—A gravity die-cast cylinder head, showing cooling fins.

An aluminium alloy with 10% silicon and 0·5% magnesium has been used in America and another alloy with 8% magnesium has been used where high strength coupled with ductility are needed, though at the expense of castability. There is an alloy with 10% magnesium in use in this country, having a tensile strength of about 18 tons/sq. in. and an elongation figure of about 12%, this alloy unfortunately is difficult to die cast. Another aluminium-magnesium alloy is D.T.D. 165 with 3–6% magnesium ; this is used in gravity die casting.

Much still remains to be done in developing pressure die-casting alloys that will anodise and take a tinted finish. Unfortunately the requirements of pressure die casting and successful anodising seem to be opposed. A good pressure die-casting aluminium alloy needs a high-alloy content, which for anodising to be followed by tinting a low alloy content is needed.

Before leaving the alloys which are die cast, mention should be made of the use of practically pure aluminium in the making of pressure-cast rotors. Normally the unalloyed metal cannot be pressure cast owing to hot shortness. However, the numerous inserts contained in a rotor, back up the metal as it solidifies and thus enable a satisfactory casting to be made. The use of die casting provides the advantage of one piece construction and thus a longer life is assured, coupled with less noise than in the fabricated type.

The laminations are stacked in the die-casting die ; molten aluminium is then injected and the casting with its numerous inserts is removed from the die. After the die-casting process a keyway is broached, the rotor shaft pressed into the rotor which is then straightened into correct alignment in a press. The outside diameter is then turned and the rotor balanced. Such use of practically pure aluminium is a fairly recent development ; in the past the cast rotors have been made from an aluminium-silicon alloy with 2½% silicon, and even from the L33 composition.

The writer is very grateful to Messrs. Birmingham Aluminium Casting Co., Ltd., for their help in connection with this article. The illustrations have been provided by them and by Messrs. Fry's Diecastings, Ltd.

Staff Changes and Appointments

MR. ELLIS HUNTER has been re-elected President of the British Iron and Steel Federation for the year 1948. Mr. Hunter, who is deputy chairman and managing director of Dorman, Long & Co., Ltd., succeeded to the Presidency on the death of Sir Allan Macdiarmid in August, 1945, and was re-elected for the year 1947.

MR. G. H. LATHAM, President-elect in 1947, has been appointed to the office of Past President, following the resignation of Sir James Lithgow, who had held the office since 1945. Mr. Latham is chairman of Whitehead Iron & Steel Co., Ltd., and a member of the Iron and Steel Board.

MR. NEVILLE H. ROLLASON has been appointed President-elect for the year 1948. He is managing director of John Summers & Sons, Ltd., and is also a director of the United Steel Companies, Ltd., and is chairman of the British Steel Producers' Conference ; he is also on the board of B.I.S.C. (Ore), Ltd., and the Council of the British Iron and Steel Research Association.

MR. H. P. R. SCOTT has been appointed joint managing director of Messrs. Thomas Summerson & Sons, Ltd. and Messrs. Summerson's Foundries, Ltd., of Darlington. Mr. Scott is very well known in the steel foundry industry, and during the latter part of the war he was Director for Steel Castings at the Ministry of Supply, Iron and Steel Control.

LT.-COMDR. G. W. WELLS has been appointed joint general manager with MR. W. B. BAXTER, of the Appleby-Frodingham branch of The United Steel Companies, Ltd. Further appointments include : MR. A. ROBINSON, who becomes technical consultant and a member of the Appleby-Frodingham board ; ENGR. REAR ADMIRAL C. W. LAMBERT becomes general works manager ; and MR. A. JACKSON, MR. G. D. ELLIOT and MR. W. GEARY are appointed works managers. MR. K. PATERSON takes over Engr. Rear Admiral Lambert's duties as chief mechanical engineer, and MR. J. L. GASKELL is appointed chief electrical engineer.

REAR-ADMIRAL M. S. SLATTERY, C.B., R.N., has been appointed to the board of Short Bros. & Harland, Ltd. Until his retirement Rear-Admiral Slattery was Vice-Controller (Air) in the Admiralty and Chief Naval Representative, Ministry of Supply.

MR. N. E. KEARLEY, A.M.I.E.E., deputy director of the Council of Industrial Design, has resumed duty with the Ministry of Supply—Electrical Plant Division—having completed his period of loan to the Council.

MR. J. R. TOMLINSON has been appointed agent in charge of the Cleveland ironstone mines of Dorman Long & Co., Ltd. Joining the Company's service in 1928, Mr. Tomlinson has been manager of the Lumpsey mine since 1932. The Company also announce that MR. W. I. E. HICKMAN has been appointed agent in charge of the Company's limestone quarries and Burley ironstone quarry, and Eston mine. These changes follow the death of Mr. Harry Palmer, agent in charge of the Company's ironstone mines and quarries for many years.

MR. H. BUTTERWORTH, Assoc.M.C.T., A.M.I.E.E., sales manager of the Motor and Industrial Control Departments of the Metropolitan-Vickers Electrical Co., Ltd., has left the Company to take up an executive appointment with Edison Swan Electric Co., Ltd. From January 1st, MR. H. BOYD BROWN, B.Sc.(Eng.), will be sales manager, Motor Department, and MR. C. H. DE NORDWALL, D.F.H., M.I.E.E., sales manager, Industrial Control Department ; MR. F. R. MASON, B.Sc.(Tech.), A.M.I.Mech.E., will succeed Mr. Brown as principal representative at Trafford Park of the M-V. Export Company.

MR. J. M. SURRALL, general commercial manager, has been appointed a Director of the Tube Investment subsidiary company, Simplex Electric Co., Ltd., of Oldbury, Birmingham. Mr. Surrall joined the original Simplex Steel Conduit Co., Ltd., in 1903, and was appointed manager of the electrical Heating and Cooking Department in 1912, and became sales manager in 1922. On the formation of Simplex Electric Company in 1932, he was appointed joint sales manager, becoming general commercial manager in 1946.

Methods of Testing Metallic Abrasives

By J. E. Hurst, D.Met., J.P.

The actual behaviour of metallic abrasives in service is the final test of their quality, but service tests are not always easy to carry out, and convincing and conclusive results from such tests are difficult to obtain. Many variables are involved and in this paper, given by the author at a recent meeting of the Midlands Branch of the Institute of Vitreous Enamellers, he shows that, with a knowledge of service requirements, laboratory facilities, laboratory systems of testing can be developed to provide results which enable an appraisal of the service behaviour of metallic abrasives.

METALLIC abrasives are used extensively in all the various forms of machinery for the cleaning and treatment of the surfaces of various articles by blasting processes. They are manufactured in two forms and frequently spoken of as chilled shot and grit, respectively. By metallic shot is understood the rounded more or less spherical particles of metallic material in contradistinction to the angular or cornered particles possessing a multiplicity of cutting edges. This latter form is referred to as metallic grit or cornered grit. Apart from their use in shot blasting machinery or mechanically operated machines of the Wheelabrator type for various cleaning operations, metallic abrasives of this type find a use in a variety of special applications, as for example, stone sawing, cutting and polishing, well boring and drilling, and the development of special surface finishes on articles of various descriptions in a variety of materials in addition to metals. Such abrasives, for example, have been used for the preparation of surfaces on woods and bricks.

An important special application of the shot blasting treatment has been developed over the last few years in the surface treatment of springs particularly, and other parts highly stressed in service with the object of improving their resistance to fatigue failure. It is well known that the initiation of fracture in fatigue failures is conditioned, to a considerable extent, by the character and the stress conditions in the surface of the particular part. The peening action on the surface arising during shot blasting in many instances has been found to have a profound effect in bringing about surface conditions highly resistant to fatigue failure.

Each and every one of these operations enumerated are operations of considerable importance in the engineering and metallurgical industries. In a like manner the metallurgical character and the properties of metallic abrasives, shot and grit, are matters of equal importance, and their study and the establishment of methods of examination and testing is fundamental to the maintenance and improvement of the efficiency of this material in its various uses.

For these many purposes, both shot and grit are manufactured and supplied in a range of sizes from finely crushed material of less than 100 mesh up to comparatively coarse grades. It is found in practice that different grades or sizes are suitable for different classes of work and the production of different types of surface finish.

The requirements of shot and grit may reasonably be expected to differ according to the particular purpose for which they are used. For example, it may be expected that the operations of stone sawing and cutting will demand characteristics in the abrasives different from those required for the operations in the surface preparations of castings and sheets for vitreous enamelling. Whatever the service, however, the performance of abrasives in service is estimated in terms of the character and quality of the work done and their length of life. The former is fundamentally difficult to express in numerical terms in any individual case, and is commonly an expression of opinion on the part of the operators and managements, reinforced of course, by their knowledge and experience of their particular requirements and often by comparative methods based on work done with standards known to be acceptable. The length of life of abrasives can be expressed in a variety of ways and the one which has the obvious appeal is the amount of abrasive used in relation to the quantity of articles treated.

Whilst it cannot be gainsaid that the final test of the quality of metallic abrasives, whether shot or grit, lies in their actual behaviour in service, it is equally true to say that service tests are not always easy to carry out and it is generally difficult to obtain convincing and conclusive results from such tests. In service, apart from the abrasive itself, there are a large number of factors which have an influence on performance. The design and type of the blasting machine, the technique of the machine, operation and such considerations as air pressure and velocity in mechanical machines, nozzle type, shape and condition, angle of impingement and distance of the shot stream from the work are amongst the factors which have been shown to be important.[1, 2]

In individual cases by careful control such service tests can be made to provide important information and comparative results of value.[3] Perhaps the greatest single difficulty associated with service tests arises from the fact that such tests are almost always of comparatively long duration. On all these various grounds alternative methods of testing, particularly laboratory tests become matters of considerable importance.

Metallurgical knowledge teaches us that the properties of hardness, strength, toughness and, in fact, all the physical and mechanical properties of metals are capable of substantial variation according to the chemical composition and the thermal treatment to which the metal has been subjected during manufacture and it would not be unexpected to find that metallic abrasives under any given conditions of service could reveal differences in service behaviour bearing some relationship to their physical and mechanical properties, resulting from their chemical composition and thermal treatment in manufacture.

1 F. W. Neville, *Proc. I.B.F.*, **19**, 555–575.
2 J. H. D. Bradshaw, *Proc. I.B.F.*, **29**, 565.
3 J. E. Hurst and W. Todd. "An Investigation into the Use of Metallic Abrasives," I.V.E. Annual Conference, 1938.

Chilled Shot and Grit and its Constitution

Modern metallic abrasives are manufactured from chilled iron with carbon contents which may lie within the range 2·75% to 3·5%. In all the existing processes the iron used is chilled by processes in which the molten metal is granulated or disintegrated in small drops or fine globules which are immediately quenched in water. To a large extent due to smallness in size of the particles of molten iron as quenched the nature of this chilling operation may be very severe. The severity of the chilling or quenching of individual particles, in addition to depending upon their size, depends also upon the temperature of the molten metal from which they are quenched, and the effectiveness of the quench, e.g., the quickness with which they are immersed and the nature of the quenching medium. The conditions of molten metal temperature, the speed of quenching and the nature of the quenching medium may vary as and between one process of manufacture and another with the consequent effect of variation in the severity of the chilling operation. This in turn affects the constitution of the shot or grit as revealed by the micro-structure. For this reason the examination of the structural character is regarded as of considerable importance in the methods of testing metal abrasives.

Under conditions of very drastic chilling very fine grained structures are generally obtained, and on examination of polished and etched sections under the microscope high degrees of magnification are necessary in general to completely resolve the structure. The structure of drastically chilled material etched with Nital or Picric Acid shows a mass of hard carbide and phosphide, white etching constituents embedded in a dark etching ground mass essentially martensitic in character together with some austenite. Typical examples are shown in Figs. 1 and 2, which show respectively a specimen at a magnification of 120 and 1,200 diameters respectively. The structure of the ground mass is very frequently a guide as to the severity of the quenching, and incidentally the hardness and toughness. With less severe quenching the presence of austenite and martensite diminishes, the structure tending to become more pearlitic in character.

Irregularity of size of the granulated material during quenching is responsible for variation in character of the structure observed in examining individual grains of abrasive. This is revealed generally through the extent of the martensitic character which is affected by the quenching conditions and the tendency to more or less austenite. The presence of small amounts of elements such as nickel, copper, chromium, molybdenum, etc., occurs very frequently in the materials used in the present day manufacture of abrasives and according to their nature and amount they can exert quite a marked influence on the tendency towards martensitic and austenitic characteristics under the drastic quenching conditions. The total amounts of such residual elements to-day may quite easily exceed 0·5% and amounts in excess 1·0% are by no means uncommon.

With the knowledge of the effect of low temperature heat-treatment on material of this character in developing maximum hardness and strength conditions certain manufacturers have adopted heat treatment in the process of manufacture. Apart from its effect on hardness and strength heat treatment also tends to improve considerably the uniformity of the structure of the abrasive, a factor which makes for improved behaviour in service. Marked variation in structural character of individual grains of abrasive may be taken as an indication of the absence of heat-treatment during manufacture.

The procedure followed in the preparation of specimens for micro-examination is straightforward, in that a number of grains are embedded in bakelite and polished suitable for etching and examination in the usual way.

Hardness

The hardness of actual grains of abrasive, either shot or grit, can be measured best by diamond hardness testing using either the Firth, Vickers or Rockwell hardness testing machines. In the Firth or Vickers machines quite low indenting loads can be applied, thus avoiding the difficulty of fracture of individual grains. Specimens can be mounted in white metal or bakelite and ground and polished to provide flat surfaces suitable for hardness testing. A typical test specimen showing a magnified view of the diamond hardness impression is shown in Fig. 3.

The hardness test can prove to be useful in evaluating the quality of metallic abrasives. Uniformity of hardness value in a number of individual particles from any one sample is an excellent indication of care in manufacture and the possibility of treatment having been applied to secure uniformity.

A few results extracted from various investigations in our laboratories are assembled in Table I. The mean hardness values recorded in this table are those determined in the complete investigation and are not

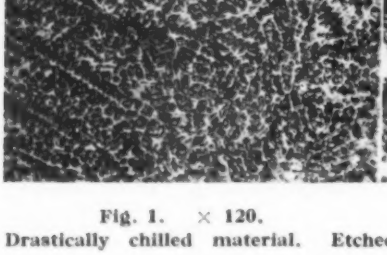


Fig. 1. × 120. Drastically chilled material.

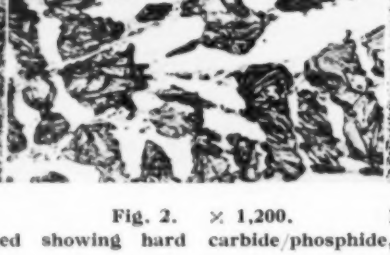


Fig. 2. × 1,200. Etched showing hard carbide/phosphide, martensitic/austenitic structure.

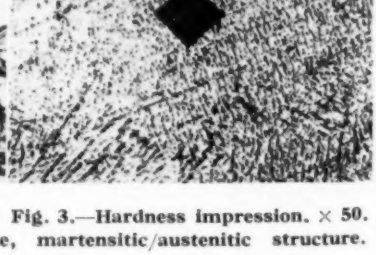


Fig. 3.—Hardness impression. × 50.

TABLE I.—VICKERS DIAMOND HARDNESS DETERMINATIONS ON SHOT AND GRIT SAMPLES.

No.	Type	Determinations							Mean	Source
47/1	Shot	847	824	824	824	724	665	564	753	European
47/1	Grit	858	858	821	803	803	715	464	760	European
47/6	Grit	828	824	803	780	760	700	640	771	European
—	Shot	645	642	642	642	606	545	514	600	South American

necessarily the mean of the seven determinations shown in the table. These determinations are examples of the type of hardness variation encountered in individual samples. Samples having a mean hardness of over 750 are found to contain particles substantially lower, as for example, the grit sample 46/1 with a low figure of 464. The table also includes a sample showing a lower mean hardness of 600. In comparison with these figures the mean hardness of grit manufactured by the Company with which the author is associated lay between the values of 844 to 920 for the period June 1945 to August 1946.

TABLE II.—MEAN HARDNESS VICKERS NO. OF VARIOUS SHOT AND GRIT SAMPLES.

No.	Type	Source	Mean Vickers Hardness No.
G.H. ..	Grit	British 1945	920
S.A.	Shot	British 1936	1,016
S.C.	Shot	British	999
S.D. ..	Shot	German	912
G.F. ..	Grit	German	1,048
S.E.	Shot	American	905
G.G.	Grit	American	920
G.B.	Grit	American	883

In Table II is a selection of mean hardness determinations of samples of the products of British and foreign firms over the last 10 years. Hardness values of over 1,000 are recorded and in general it will be seen that the values can be regarded as in excess of a round figure of 850.

Specific Gravity and Density Determinations

The determination of the specific gravity can be carried out conveniently by the density bottle method. and in many investigations can prove to be of value. In the case of shot in particular, it may prove a useful guide as to the extent of unsoundness. It does happen in hardness determinations on shot samples that low results are obtained due to the existence of unsoundness cavities in the centre of each grain. Apart from the existence of porosity a higher specific gravity indicates a proportionately higher energy content in moving particles of abrasive of identical size at the same velocity. In a series of determinations from the author's laboratories previously published, values[4] of 7·40 to 7·53 were reported in samples from various sources showing a difference of 2% approximately from the lowest to the highest result. The further values recorded in Table III show some results lower than these figures of 7·26 approximately being recorded. In both these cases, the presence of unsoundness was detected on examination under the microscope, and it is quite likely that in either grit or shot of normal manufacture values of this low order are indicative of unsoundness.

There are two other density determinations which may provide useful information in the case of investigation. They are respectively, the bulk density or packed density, and the loose packing density or loading weight. A simple method of making bulk density determinations can be carried out by the use of a graduated glass tube closed at one end into which the samples of shot or grit can be poured. This tube

[4] J. E. Hurst and J. H. D. Bradshaw, *Proc. I.B.F.*, **31**, 660.

TABLE III.
MEAN SPECIFIC GRAVITY OF VARIOUS SHOT AND GRIT SAMPLES.

No.	Type	Source	Mean Specific Gravity	Bulk Density grs. per c.c.	Loose Packing Density grs. per c.c.
G.H.	Grit	British 1945	7·493	4·20	3·74
S.A.	Shot	British 1936	7·500	4·14	4·03
S.C.	Shot	British	7·455	4·10	3·80
S.D.	Shot	German	7·450	4·30	3·88
G.F.	Grit	German	7·262	4·50	3·90
S.E.	Shot	American	7·330	4·18	3·88
G.G.	Grit	American	7·413	4·30	3·95
G.B.	Grit	American	7·265	4·57	3·88

containing the sample is tapped longitudinally until it settles to a level which remains constant even after further tapping. The volume of the packed sample is measured and knowing the initial weight the bulk density in grains per cubic centimetre can be calculated. In the author's laboratory a graduated tube 2 metres long and 1 centimetre diameter is used with a sample of an average weight of 350 grammes.

The loose packing density is determined by allowing the shot or grit to flow freely from a smooth funnel at a fixed height over a container of a known volumetric capacity. The surplus over that required to fill the container is skimmed off by drawing a knife carefully over the top of the container. The weight of grit which completely fills the known volume of the container expressed in grams per cubic centimetre is the loose packing density or loading weight.

An important factor in the behaviour of abrasives in service, particularly in the case of angular material or grit, is the particle shape. Considerable thought and investigation has been devoted to the question of the appraisal of the shape factor of irregular shaped particles of all kinds of material, and there are quite a few experimental methods devised for the determination of data which will allow of some aspect of this shape factor being expressed numerically. A difference in shape of particles would be expected to lead to a difference in packing characteristics and hence it may be expected that these packing density figures may be helpful in this direction.

The values given in Table III for these density determinations are typical of those obtained with shot and grit of normal production. It is of special interest to examine the figures for the two samples "SA" and "SC." Whilst the Bulk Density values are nearly identical, the loose packing density figures are sizeably different. These two samples are of different manufacture, but very closely alike in size as revealed by sieve test, being 29·8 and 24·8 through 7 and retained on 9 mesh respectively, and 70·2 and 75·2 retained on 7 mesh. The marked difference in loose packing density is an indication of difference in shape factor between these two samples.

Examination of Shape

The shape of particles may be studied better by individual examination under the binocular microscope than by direct magnification with a single tube microscope. It is a matter of some difficulty to record photographically with complete satisfaction the angularity of grit, owing to the difficulty of conveying an accurate rendering of the impression of depth. Figs. 4, 5 and 6 show some of the characteristics of the specimens referred to in Table III.

These illustrations serve as examples of the type of photographic record of shape obtainable and their value in the critical examination of this material. The

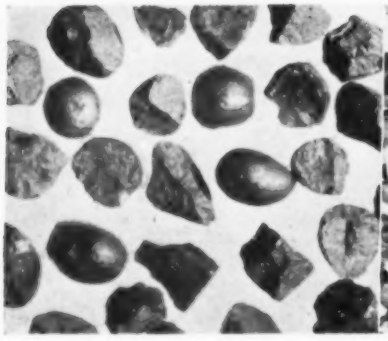


Fig. 4.—German grit.

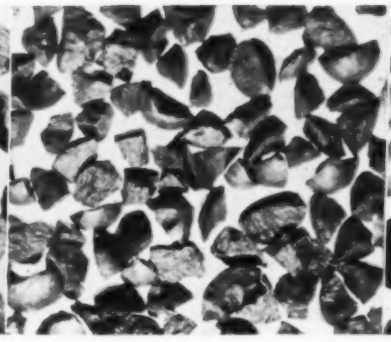


Fig. 5.—U.S.A. grit.

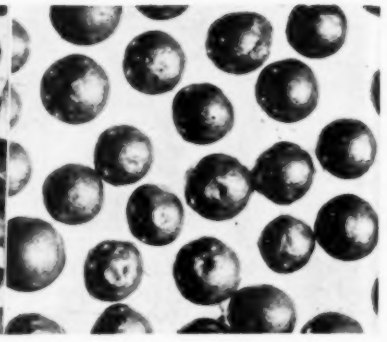


Fig. 6.—German shot. × 4

uniform particle shape of "G.G.," Fig. 5, is quite noticeable. The photograph of the shot "S.D.," Fig. 6, reveals sinking characteristics in the individual particles.

A common method of detecting the presence of shot in admixture with grit is the use of an inclined plane. A quantity of grit is placed on a smooth board which is raised gradually from a horizontal position until an angle is attained at which the rounded particles tend to flow down the inclined plane.

Strength Properties

It is difficult to conceive of a method for the direct determination of the simple strength properties of material in the form of abrasives whether angular or round. The strength properties likely to be of interest are the ultimate breaking strength, the resilience value and perhaps the modulus of elasticity. These properties are of interest insofar as they can throw light on the resistance to disintegration of abrasives under the various service conditions under which it is called upon to perform. Whilst investigation work can be done and, in fact, has been done in the author's laboratories on this material in sizes suitable for the provision of test pieces for use in various types of testing machines, it is by no means certain that such work gives a true indication of the properties of this same material after undergoing the treatments involved in the manufacture of abrasives.

As a control test in manufacture it has been common practice to make a somewhat arbitrary determination of the crushing strength. In general, the method followed has been to select a suitable size of spherical particle and determine the load required to crush the particle. In practice, an individual manufacturer has been able to draw up a list of crushing loads for different sizes of shot to use as a standard of reference. Another method designed to appreciate the toughness of the material takes the form of a drop test or impact test in which a known weight is dropped on to individual specimens of shot of known diameter. In this method the height required for this known weight to fracture the shot in a single blow is finally arrived at and used as a comparative measure of the toughness of the shot.

Toughness and Crushing Index

This impact method of testing has been expanded in the author's laboratory to provide a crushing index which shall be applicable to irregular particles as in the case of grit.

It is very desirable to be able to express "quality" of a grit mathematically in terms readily comparable and easily determined by a laboratory test. The crushing Index Test described as follows, is put forward as a type of "toughness" test, the results of which can be expressed by a number.

The idea was originally based upon the well-known Shatter Index determination, as applied to furnace cokes. The metallic abrasive is graded on standard sieves before and after being subjected to a standard crushing treatment. The change in particle size during the test is taken as a measure of that property of grit which we call familiarly "The Toughness."

The apparatus shown in Fig. 7 consists of a small hardened steel mortar with a central hole 1¼ in. deep, and of diameter sufficient to take a sliding hardened steel pestle 1¼ in. diameter by 2 in. long. This assembly is mounted between vertical parallel bars on a firm metal base. A weight of 4 lbs. secured by a movable hook 14 in. above the head of the pestle can, when required, be allowed to slide relatively unimpeded down the parallel bars to give an impact on the pestle. The weight can be pushed back by hand and re-secured by the hook prior to a second descent.

A graded sample of 10 gms. of grit is taken for this test, and approximately one-third is spread in the bottom of the mortar underneath the pestle. The weight is allowed to descend and make an impact on to the pestle head in all ten times per each batch of grit. The crushed grit is removed from the mortar and when each third of the sample has been similarly

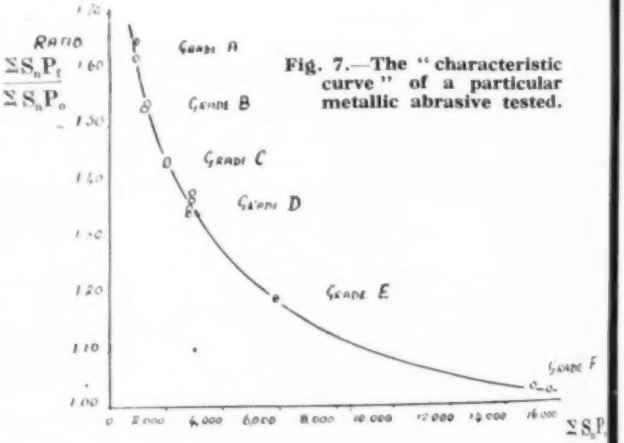


Fig. 7.—The "characteristic curve" of a particular metallic abrasive tested.

treated, the whole is regraded in standard sieves. The figures obtained during the initial and final gradings are used for the calculation of the Crushing Index of the Grit.

Notes on the Evaluation of a "Crushing Index"

A typical result of standard sieve gradings before and after crushing in the test apparatus is given in Table IV.

TABLE IV.—TYPICAL GRADINGS BEFORE AND AFTER CRUSHING. B. & F. GRIT—GRADE "D."

Sieve Sizes	Before Crushing, %	After Crushing, %
+ 18	9·0	4·0
+ 28	88·0	78·0
+ 60	3·0	12·0
+ 150	Nil	6·0

The evidence of crushing from the Table is difficult to interpret quantitatively and some thought was given to the possibility of calculating from sieve gradings a simple number or index which would be characteristic of the grit tested. The method finally chosen was to assume that at any sieve size the product of the mesh aperture number, multiplied by the percentage of grit remaining on that sieve, was roughly proportional to the number of particles of grit of that size. The total number of particles of grit in any sample will, therefore, be proportional to the summation of the products of mesh size × percentage for the sieve covering that grade of grit :—

$$\text{i.e., } N = \Sigma\ K\ (S1P1 + S2\ P2 + \ldots . Sn\ Pn)$$

Where N = number of grit particles in sample.
K = constant of unknown value.
S = sieve size number.
P = percentage retained on each sieve.

If now the sample is regraded on the same sieves after crushing in the apparatus, the increased number of particles produced may be determined again by the above expression. The ratio of number of particles sent after crushing to the number of particles originally present is then related to the "toughness" factor of the grit, and may be called a "crushing index."

$$\text{i.e., } CI = \frac{Nf}{No} = K\ \frac{\Sigma\ Sn\ Pf}{\Sigma\ Sn\ Po}$$

Where CI = "Crushing Index."
Sn = Sieve Sizes.
Po = Original percentage on each sieve.
Pf = Final percentage after crushing on each sieve.
No = Number of particles of grit in orig. sample.
Nf = Number of particles of grit after crushing.

As an example of the way in which the "crushing index" of a grit may be determined, the method of working is shown in Table V, using the "D" grade grit grading figures in Table IV.

TABLE V.—THE DETERMINATION OF "CRUSHING INDEX."

Sn	Po	Pf	SnPo	SnPf
18	9·0	4·0	162	72
28	28·0	78·0	2464	1284
60	3·0	12·0	180	720
150	Nil	6·0	—	900
			Σ Sn Po 2806	Σ Sn Pf 3876

$$CI = K\ \frac{\Sigma\ Sn\ Pf}{\Sigma\ Sn\ Po}$$

$$= K\ \frac{3876}{2806} = 1{\cdot}37$$

N.B.—The constant K is assumed to be constant for the apparatus and method of working, and can be neglected.

A number of check determinations of CI for the same sample of "D" Grade Grit gave values ranging from 1·34 to 1·37.

Variations in "Crushing Index" with Grit size variations.—The "crushing indices" of Bradley and Foster grit grades A to F were determined. The value of the "index" was found to depend upon the intial grade, i.e., grade "A" gave 1·64, and grade "F" gave a figure of 1·03. Intermediate grades gave values which could be plotted in a smooth curve, as shown in Fig. 7. This curve has been called the "characteristic curve" of the particular metallic abrasive being tested.

The use of the Characteristic Curve.—Check experiments using the standard method and apparatus shown in Fig. 8 confirmed that the characteristic curve could be determined with fair precision of a particular type of metallic abrasive. Once determined, the curve can be used to assess the quality of any other abrasive. It is not necessary for the unknown sample to conform to any one of the standard grades of grit (i.e., "A" to "F"), as any grading can be accommodated by the smooth curve between the standard grades.

Fig. 8.—Standard apparatus for checking "characteristic curve."

The method of working to check up on the quality of a grit is given below :—

(1) The grit is graded on standard sieves (Grades 7, 9, 12, 18, 28, 60, 150 and 200).
(2) The summation of the products of sieve number by percentage retained by each is obtained, i.e., Σ Sn Po.
(3) The standard crushing test is carried out and the grit is regraded to obtain a second summation of products, i.e., Σ Sn Pf.

TABLE VI.

COMPARISON: POTTER & SOAR STANDARD—V-B.S.I.-V-I.M.M. SIEVES.

Mesh	S.W.G.			Aperture			Screening Area %		
	Potter and Soar	B.S.I.	I.M.M.	Potter and Soar	B.S.I.	I.M.M.	Potter and Soar	B.S.I.	I.M.M.
4	19	None	None	·210	None	None	71	None	None
5	20	15½	12	·164	·132 4/125	·100	67	44	25·0
6	21	17	None	·135	·1107 6/125	None	65	44	None
7	22	18	None	·115	·0949 1/10	None	65	44	None
8	23	18½	16	·101	·0810 1/12	·062	65	42	24·6
9	24	None	None	·089	None	None	64	None	None
10	25	20½	18	·080	·0660 1/15	·05	61	44	25·0
12	26	22	19	·065	·0553 1/18	·0416	58	44	24·92
14	27	23	None	·055	·0474 1/21	None	56	44	None
16	27	23½	21	·0461	·0395 1/25	·0312	54	40	24·92
18	28	24	None	·0408	·0336 1/30	None	54	36	None
20	28	None	23	·0352	None	·025	50	None	25·0
22	29	26	None	·0319	·0275 1/36	None	49	36	None
24	29	None	None	·0281	None	None	45	None	None
25	None	27	None	None	·0236 4/170	None	None	35	None
28	31	None	None	·0241	None	None	46	None	None
30	32	29	27	·0225	·0197 1/50	·0166	46	35	34·8
36	33	31½	None	·0178	·0166 1/60	None	41	36	None
40	34	None	30	·0158	None	·0125	40	None	25·0
40	None	34½	None	None	·0139 1/72	None	None	38	None
50	36	None	33	·0124	None	·0100	38	None	25·0
52	None	36	None	None	·0116 4/345	None	None	37	None
60	37	37	35	·0099	·0099 1/100	·0083	35	35	24·8
72	None	38½	None	None	·0083 1/120	None	None	36	None
80	39	None	38	·0073	None	·0062	34	None	24·6
85	None	40	None	None	·0070 1/142	None	None	35	None

(4) The ratio $\frac{\Sigma \text{ Sn Pf}}{\Sigma \text{ Sn Po}}$ is calculated

(5) Reading from the "characteristic curve" of the standard range of Bradley and Foster samples and using the Σ Sn Po values determined in item (2), the derived ratio may be obtained and the experimentally observed ratio (item 5) for the unknown sample may be compared. If in each case the ratio or "crushing index" is the same, then the "toughness" quality of the sample is clearly the same as that of the standard range of grits.

The "characteristic curve" may also be used to assess the quality of other makes of grit, since a higher crushing factor for any particular grade (or Σ Sn Po value) would signify a lower toughness. Conversely, a low crushing factor denotes superior toughness and absence of particle break-up during test.

Grade Analysis

The examination of both shot and grit for grading is carried out using laboratory sieving machines of the Rotap or Inclyno type equipped with sieves. In this connection, it is important to draw attention to the fact that the screening of both shot and grit is carried out utilising the range of mesh sizes of cloth produced by the screen cloth manufacturers. There are important differences between the range of commercially available mesh sizes, and the range of mesh sizes listed in the B.S.I. and I.M.M. standards. It is also important to draw attention to the fact that in any given mesh size of cloth, the aperture size is determined by the diameter of the wire used in the cloth, and because of this there are differences in aperture size between the commercial standard cloths of most makers and those listed in the B.S.I. and I.M.M. standards.

TABLE VII.

	A	B	C
Grade Analysis, Oversize + 28	1·5 %	2·7 %	0·5 %
Size 28 + 60	94·1 %	88·0 %	98·0 %
Undersize 60	4·4 %	9·3 %	1·5 %
Dust Oxide and Fines 240..	0·01%	0·26%	0·02%
True Specific Gravity (Density)	7·47 grs./c.c.	7·40 grs./c.c.	7·44 grs./c.c.
Bulk Density..	4·04 grs./c.c.	4·05 grs./c.c.	4·06 grs./c.c.
Loose Packing Density..	3·68 grs./c.c.	3·46 grs./c.c.	3·90 grs./c.c.
Graded 28 + 60 Loose Packing Density	3·82 grs./c.c.	3·44 grs./c.c.	3·86 grs./c.c.
Chemical Analysis			
Total Carbon	2·95%	3·02%	2·81%
Silicon	1·05%	1·49%	1·65%
Manganese	0·20%	0·14%	0·36%
Sulphur	0·25%	0·24%	0·21%
Phosphorus	1·05%	1·49%	1·65%

TABLE VIII.—GRADE ANALYSIS BEFORE AND AFTER SHATTER TEST.

		A	B	C
Before	Oversize + 28	1·5	2·7	0·5
	Size — 28 + 60	94·1	88·0	98·0
	Undersize — 60	4·4	9·3	1·5
After	Oversize + 28	1·3	1·0	1·0
	Size — 28 + 28	88·2	76·5	86·3
	Undersize — 60	11·5	22·5	12·7
Differences	Oversize + 28	— 0·2	— 1·7	+ 0·5
	Size — 28 + 60	— 5·9	— 11·5	— 11·7
	Undersize — 60	+ 7·1	+ 13·2	+ 11·2

In the author's laboratory, it is the practice to equip test sieves with cloth of commercial standard sizes and sizes identical with the cloths actually used for grading purposes. For the determination of dust, oxide and fines, it very often suffices to subject the sample to sieving on a 240 mesh sieve, classifying the material passing through such a fine sieve as dust, oxide and fines. More elaborate methods can be readily devised, including magnetic separation and even chemical analysis to determine the nature of such material, should this be necessary for any particular investigation.

General Remarks

In describing these methods of testing, it is almost unnecessary to point out their importance in the routine control of the quality of these products during manufacture. It is also intended to show that with the necessary laboratory facilities and with a knowledge of the service requirements, laboratory systems of testing can be devised to obtain results which will enable an appraisal of the service behaviour of metallic abrasives to be made. Because of the many factors, such as the nature of the plant, the very often intangible character of the requirements and other variants, it is a matter of considerable importance to be able to make exhaustive and strict comparison of the quality factors of the abrasives and to be able to express these in quantitative terms.

MR. C. F. SAUNDERS, Assoc.M.C.T., A.M.I.E.E., has been appointed chief engineer of Metropolitan-Vickers Welding Department in succession to Mr. H. West, who has relinquished this appointment in order to devote full time to his duties as assistant to Chief Electrical Engineer. Mr. Saunders joined the Company as a school apprentice in 1916. Following his apprenticeship, broken by war service in the R.E. (Signals), he joined the Motor Engineering Department of the Company in 1922. After a period in Motor Sales Department he returned to Motor Engineering Department as chief cost engineer, which position, with increasing responsibilities, he has retained until now.

DR. ROBERT CHARLES GOODING WILLIAMS, M.I.E.E., M.I.Mech.E., has been appointed Chief Engineer of Philips Electrical, Ltd., to advise the managing director on all technical matters. Dr. Williams comes direct from the North American Philips Company, Inc., of New York, U.S.A., where, as an executive engineer, he gained experience in American industrial methods and developments in the electrical and allied fields, and acquired an intimate knowledge of American business administration and manufacturing technique. He is retaining his connection with the American group as technical adviser to North American Philips.

A Critical Examination of a Perchloric Acid Colorimetric Method of Analysis for Chromium in Carbon and Low Alloy Steel

Report of The Methods of Analysis Committee of the Metallurgy Division of The British Iron and Steel Research Association

Based on the colour intensity of dichromate in perchloric acid solutions containing ferric iron, a colorimetric method for low contents of chromium in steel has been investigated. The method is very simple and speedy, but several factors exert a marked effect on the colour intensity of the solution and is not considered suitable as a standard method. Under routine conditions, however, the method has obvious advantages and it is recorded here for those wishing to use it.

Introduction

A METHOD for the colorimetric determination of low contents of chromium in steel† has appeared, in which an interesting principle is adopted. In perchloric acid solution, the presence of ferric perchlorate intensifies the colour of the dichromate ion to a degree which enables accurate colour measurements to be made of relatively low dichromate concentrations by absorptiometric means.

As the speed and simplicity of this method were such as to offer distinct advantages over previous colorimetric procedures, and as the Residual Metals Panel of the Analysis Sub-Committee (I.S.I.) was at that time investigating procedures for low contents of chromium in steel, it was decided to carry out trials. The preliminary experiments were definitely promising, although certain members reported difficulties in the operation of the method. Further work confirmed these somewhat conflicting experiences, so that it became apparent that a more detailed investigation of the conditions would be necessary in order fully to ascertain the applications and limitations of this method.

Although the conclusion drawn from the investigation was that the method could not be recommended as a standard procedure, the method was found to have definite applications under closely controlled conditions. It was also considered that the investigatory work carried out could usefully be placed on record for the guidance of those wishing to use the method under routine conditions.

The Residual Metals Panel of the Analysis Sub-Committee (now merged in the Analysis Sub-Committee of B.I.S.R.A.) was constituted as follows :—

Mr. B. Bagshawe, The Brown-Firth Research Laboratories ; Mr. L. E. Gardner, Messrs. Edgar Allen and Co. Limited ; Mr. S. Harrison, Messrs. Kayser Ellison and Co. Ltd. ; Mr. J. D. Hill, The Bragg Laboratory ; Mr. A. P. Lunt, The Parkgate Iron and Steel Co. Limited ; Mr. G. E. Speight (Convenor), The United Steel Companies Limited.

This report is presented as a collaborative examination by the above Panel.

TABLE I.—THE EFFECT OF PERCHLORIC ACID CONCENTRATION.

Perchloric Acid Addition (Sp. gr. 1·54 ml.)	Chromium %	Absorption Value 0·50g. Iron		Actual Spekker Readings 1·00g. Iron	
		Covered beaker	Reflux condenser	Covered beaker	Reflux condenser
15	0·10	—	—	0·81	0·805
20	0·10	—	—	0·82	0·805
25	0·10	—	—	0·81	0·79
10	0·20	—	—	0·32	—
12	0·20	—	—	0·41	—
15	0·20	—	—	0·47	—
18	0·20	—	—	0·48	—
20	0·20	—	—	0·485	—
25	0·20	—	—	0·475	—
30	0·20	—	—	0·35	—
8	0·30	0·50	0·49	0	—
11	0·30	0·58	0·59	0·085	—
14	0·30	0·615	0·61	0·24	—
17	0·30	0·62	0·62	0·28	—
20	0·30	0·625	0·62	0·285	—
23	0·30	0·62	0·615	0·265	—
26	0·30	0·61	0·59	0·225	—
29	0·30	0·565	0·54	0·165	—
32	0·30	0·51	0·49	0·07	—
35	0·30	0·455	0·40	0	—

This report is presented as a collaborative examination by the above Panel.

Experimental

The initial work showed clearly that a number of factors had an important bearing on the success of the method. These factors, such as perchloric acid concentration, iron concentration and temperature, were investigated together with other features as are given below.

(1) Perchloric Acid Concentration

The effect of variation of perchloric acid concentration was examined by applying the procedure to synthetic tests, prepared from electrolytic iron and potassium dichromate, with varying perchloric acid concentrations in the final solution. Two series of tests of increasing chromium contents up to 0·3% were carried out, one series using samples of 0·5g. of iron, and the other of 1·0g. of iron. As the final perchloric acid concentration would depend not only on the initial acid addition, but on the degree and manner of fuming, comparative tests

* Paper MG/D/59/47 submitted by the Methods of Analysis Committee of the Metallurgy Division of the British Iron and Steel Research Association, received January, 1948.

This work was carried out by the Residual Metals Panel of the Standard Methods of Analysis Sub-Committee of the Ingots Committee of the Iron and Steel Institute. The duties of this Sub-Committee have now been assumed by the Methods of Analysis Committee of the British Iron and Steel Research Association.

† Colorimetric Determinations of Chromium in Steel. Louis Singer and Walter A. Chambers, Jr. Naval Research Laboratory. Anacostia D.C. *Industrial and Engineering Chemistry. Analytical Edition*, August, 1944, p. 507. Method given in Appendix I.

were carried out in covered beakers and under reflux condensers. The use of open beakers for the fuming operation was early discarded as leading to variability in loss of perchloric acid and consequently in the final acid concentration. A selection of typical results is given in Table I and graphically in Fig. 1.

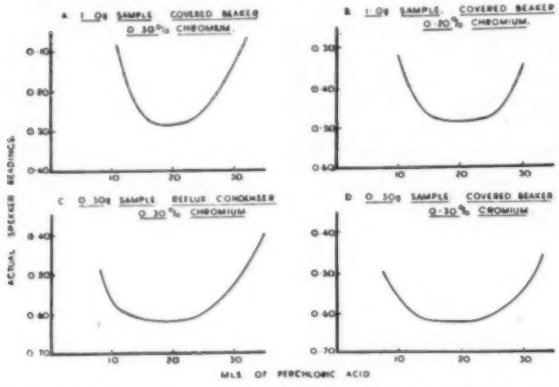


Fig. 1.—Variation of absorption with perchloric acid concentration.

A, B	Spekker Details	Filters = Ilford 601 + H503. Lamp = Mercury Vapour. Cells = 1Cm. Water : Water Setting 1.20. Temperature = 20° C.
C, D	Spekker Details	Filters = Ilford 601 + H503. Lamp = Mercury Vapour. Cells = 2Cm. Water : Water Setting 1.20. Temperature = 20° C.

The results show clearly that over a range of perchloric acid concentration, substantially constant absorption values are obtained, and that outside this range, relatively small variations in perchloric acid concentration exert a marked effect on the absorption readings. The range is slightly wider with the lower iron content, i.e., 0·5g. In almost all cases, the absorption may be regarded as substantially constant over the range 34–44% of perchloric acid (sp. gr. 1·54).

It was found also that, in practice, the permissible limits of perchloric acid concentration could be maintained by fuming according to a specified procedure in covered beakers. The use of reflux condensers to assist in ensuring standard acid concentration was considered to be an unnecessary refinement, particularly in routine applications.

The oxidation of chromium during fuming may be detected visually by a change in colour from reddish-brown to yellowish-brown. It was considered that the period of fuming would need to be based on this visual change, but tests in different laboratories showed that consistent and reproducible results were obtained after strong fuming for 3–7 minutes.

The recommended method described in Appendix II includes directions to cover the foregoing considerations.

(2) Iron Concentration

It is obvious from the principle of the method that variation in iron concentration would have a marked effect on the final absorption value. To provide quantitative data, synthetic tests containing iron varying between 0 and 1g. at each of three chromium levels, 0·1%, 0·2% and 0·3%, were carried out, with the results shown graphically in Fig. 2.

The results indicate clearly that the absorption value for a given dichromate concentration is proportional to the amount of iron present and that increased absorption resulting from a given iron content is greatest at the highest chromium level.

The immediate conclusion is that variations in iron content, as might be derived from the presence of alloying elements in the sample, would lead to low values for the chromium content of the sample when the absorption values are converted to chromium using a calibration based on 100% iron sample. With chromium contents of 0·1%, this error would be slight, e.g., a decrease of 5% in the iron content (due to other alloys) would reduce the apparent chromium figure by 0·005%. The possible error is more serious with higher chromium contents, e.g., a decrease of 5% in the iron content would reduce the measured chromium value of a sample containing 0·3% of chromium by 0·015%. The foregoing considerations apply only to sample weights of 1g.; the effects, though still present, would be less marked with 0·5g. samples.

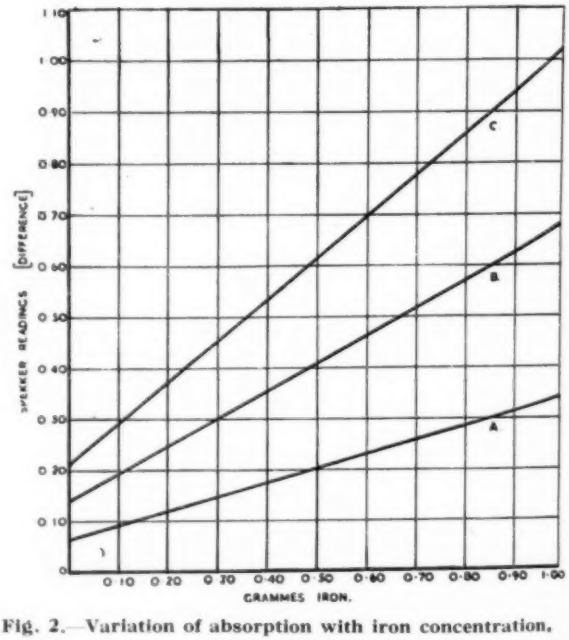


Fig. 2.—Variation of absorption with iron concentration.

Spekker Details.
Filters = Ilford 601 + H503.
Lamp = Mercury Vapour.
Cells = 1Cm.
Water : Water Setting 1.20.
Temperature = 20°C.

A. 0.0010g Chromium.
B. 0.0020g Chromium.
C. 0.0030g Chromium.

The following interpretation of these absorption effects, suggested by Mr. Harrison, is particularly interesting, in indicating a method of correcting for variation in iron content. It can be shown that there is, in effect, a two component colour system, comprising:—

(*a*) a dichromate colour in perchloric acid solution;

(*b*) an intensification of (*a*) due to iron perchlorate.

Component (*a*) remains constant for a given chromium concentration, while component (*b*) increases with the

iron content. The ratio of the two components might be expressed as follows:—

$$\frac{I_{Fe}}{I_{Cr}} = \frac{I_{total} - I_{Cr}}{I_{Cr}} = K.$$

Where I_{Cr} and I_{Fe} represent the absorption values measured in Spekker units, due to the components (*a*) and (*b*) respectively. Within normal limits of low chromium contents, i.e., up to 0·3%, the value of K is constant for a given iron content, e.g., with 0·5g. of iron K = 2 (approx.) while with 1·0g. of iron, K = 4 (approx.).

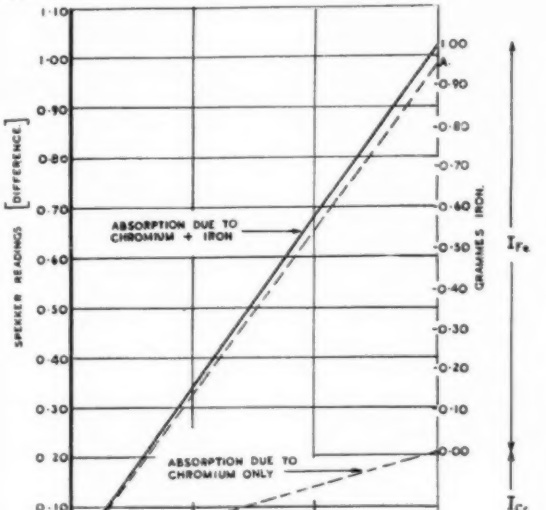


Fig. 3.—Typical calibration curve for the perchloric acid absorptiometric determination of low chromium contents.

Spekker Details.
Filters = Ilford 601 + H503.
Lamp = Mercury Vapour.
Cells = 1Cm.
Water : Water Setting 1·20.
Temperature = 20°C.

The foregoing considerations may be represented graphically as in Fig. 3. This was prepared by taking absorption measurements of two series of tests:—

(*a*) Increasing chromium contents in the absence of iron (I_{Cr}).

(*b*) Increasing chromium contents in the presence of iron (Ig.) (I_{total}).

The vertical difference in the two sets of absorption values is sub-divided into distances proportional to the iron content. The absorption values for tests in the presence of an intermediate content of iron may then be converted to chromium % by reference to a calibration curve drawn by joining the origin to the particular on level in question, e.g., an unknown test on a 1g. sample gave an absorption of 0·80 Spekker units. Referring to the calibration curve for 1g. of iron present, the chromium content would be 0·235%. The sample actually contains 4% of other major alloying elements, so that the equivalent iron content is approximately 96%. The correct calibration line would be obtained by connecting the origin with the point equivalent to 0·96g. of Fe (point A in Fig. 3). Referring the absorption reading to this new curve, the correct chromium result would be ·245%.

(3) Presence of Other Elements

In addition to the aforementioned effect due to the presence of alloying elements (i.e., the reduced iron content), it was necessary to ascertain any direct intrinsic effect due to alloying elements. Synthetic tests were carried out, therefore, on a 0·5g. sample basis using electrolytic iron together with a known amount of potassium dichromate solution, to which were added solutions of the elements in question. The normal perchloric acid method was applied and absorptiometric comparison made with similar tests without the addition of the alloying element. The results obtained are given in Table II in which the comparison is made between the theoretical chromium content and the determined value after correction for the variation in iron content.

TABLE II.—THE EFFECT OF ALLOYING ELEMENTS.

0·475g. iron for the 5% addition } All reading corrected for the
0·450g. iron for the 10% addition } iron effect.

Element	Equivalent addition %	Percentage Chromium	
		Theoretical	Determined
—	—	0·40	0·40, 0·40
—	—	0·30	0·30, 0·303
Cobalt	5·0	0·40	0·406
,, ...	10·0	0·40	0·40
,, ...	5·0	0·30	0·296, 0·303, 0·302, 0·299
Nickel	5·0	0·40	0·403
,, ...	10·0	0·40	0·392
,, ...	5·0	0·30	0·296, 0·30, 0·296, 0·296
Copper	5·0	0·40	0·398
,, ...	10·0	0·40	0·397
,, ...	5·0	0·30	0·303, 0·30, 0·299, 0·299
Manganese	5·0	0·40	0·403
,, ...	10·0	0·40	0·395
,, ...	5·0	0·30	0·334*, 0·313*, 0·299, 0·302
Aluminium ..	5·0	0·40	0·398
,, ..	10·0	0·40	0·387
,, ..	5·0	0·30	0·296, 0·303, 0·302, 0·302
Ammonium ..	5·0	0·40	0·394
,, ..	10·0	0·40	0·387
Sodium	5·0	0·40	0·403
,, ...	10·0	0·40	0·40
Potassium	5·0	0·40	0·398
,, ...	10·0	0·40	—
Molybdenum ..	1·0	0·30	0·293, 0·299
,, ..	2·0	0·30	0·286, 0·286
,, ..	5·0	0·30	0·269, 0·258, 0·195, 0·255
,, ..	5·0	0·40	0·358
,, ..	10·0	0·40	0·305
Vanadium	5·0	0·40	0·428
,, ...	5·0	0·30	0·402, 0·398

* Formation of colloidal manganese dioxide.

TABLE III.—THE EFFECT OF ACID RADICALS ON THE PERCHLORIC ACID ABSORPTIOMETRIC CHROMIUM METHOD.

Addition	Amount Added	Percentage Chromium	
		Theoretical	Determined
Hydrochloric Acid (sp. gr. 1·16)	0·10 ml.	0·40	0·23
Sulphuric Acid (sp. gr. 1·84)	0·10 ml.	0·40	0·34
Nitric Acid (sp. gr. 1·42)	0·10 ml.	0·40	0·38
Phosphoric Acid (sp. gr. 1·75)	0·10 ml.	0·40	0·27

It was realised that the acid radical of the particular soluble salt of the element used for the addition may also modify the absorption value. Synthetic tests were therefore carried out in which specific amounts of particular acids were added to solutions of iron and chromium after fuming with perchloric acid. The results are shown in Table III.

Of the four acid radicals tested, chloride and phosphate

showed the most marked interference, sulphuric acid and nitric acid showing less effect. Under normal test conditions both hydrochloric and nitric acids, if present initially, would be expelled during fuming with perchloric acid, consequently no influence on the final absorption would be obtained. Sulphate and phosphate, however, would tend to survive the fuming treatment and thereby interfere with subsequent absorptiometric readings. It is clear, therefore, that those two acids must not be employed as variants of the initial acid solvent, and that care must be taken against later accidental contamination.

The effects of alloying elements are shown in Table II. It will be seen that up to 10% of each of the metals, manganese, cobalt, nickel, copper and aluminium, exert no deleterious effect on the chromium colour measurement. High manganese contents occasionally cause trouble due to formation of colloidal substances. Both vanadium and molybdenum show interference, the former leading to high results, due apparently to the vanadate becoming a component in the colour system. The interference by molybdenum is not due to modification of the colour system, but to a change in the residual background colour on reduction with ferrous sulphate. Below 1% of molybdenum, the effect is of little significance. The presence of ammonium, sodium or potassium has no effect on the colour comparison; the latter element in high concentrations leads to slight trouble due to the precipitation of potassium perchlorate.

(4) Temperature of Solution

Absorptiometric readings of coloured solutions are prone to vary according to the temperature of the solution. Synthetic tests, containing electrolytic iron and potassium dichromate solution, were carried out as

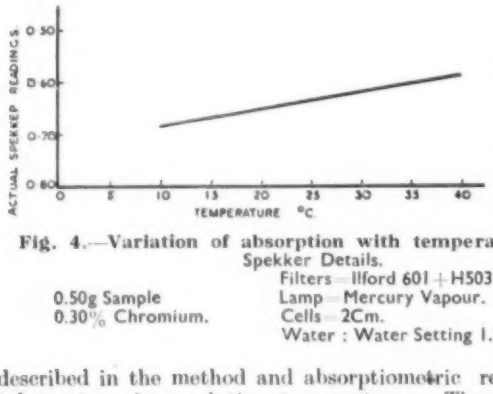


Fig. 4.—Variation of absorption with temperature.
Spekker Details.
0.50g Sample
0.30% Chromium.
Filters = Ilford 601 + H503.
Lamp = Mercury Vapour.
Cells = 2Cm.
Water : Water Setting 1.20.

described in the method and absorptiometric readings taken at various solution temperatures. The results are given in Table IV and graphically in Fig. 4.

The absorption effect due to temperature is confirmed. The extent of the effect is most marked with 1g. samples and with higher chromium contents. It is clear that to ensure accurate and reproducible results, the temperature of the solution for absorptiometric measurement must be controlled within a definite range, i.e., 20° ± 2°.

(5) Use of Ferrous Sulphate as Reducing Agent

It was observed during these experiments, that errors were caused by the use of excessive amounts of ferrous sulphate in order to obtain the reduced chromium reading. Synthetic tests were prepared as in previous

TABLE IV.
THE EFFECT OF TEMPERATURE ON THE ABSORPTION VALUE.

Temp. °C.	Iron Addition g.	Percentage Chromium		Actual Spekker Readings
		Theoretical	Determined	
10	1·0	0·30	0·27	—
20	1·0	0·30	0·30	—
30	1·0	0·30	0·33	—
10	0·50	0·30	0·27	0·69
15	0·50	0·30	0·28	0·67
20	0·50	0·30	0·295	0·65
25	0·50	0·30	0·305	0·635
30	0·50	0·30	0·315	0·62
40	0·50	0·30	0·34	0·59
10	0·50	0·40	0·37	—
20	0·50	0·40	0·40	—
30	0·50	0·40	0·425	—

TABLE V.—THE EFFECT OF FERROUS SULPHATE ADDITIONS ON THE ABSORPTION VALUE OF THE REDUCED CHROMIUM COLOUR.

Ferrous Sulphate Addition g.	Spekker Readings after Reduction	
0·04	1·17	1·175
0·10	1·105	1·105
0·20	0·95	0·97

sections and the normal method applied. After measuring the absorption of the dichromate coloured solution, varying amounts of ferrous sulphate were added and absorptiometric readings again obtained. The results are given in Table V and graphically in Fig. 5.

It will be seen that use of amounts of ferrous sulphate in excess of that specified, i.e., 0·02–0·04g., leads to higher absorption values for the reduced solution; the difference figure which relates to the chromium content would, therefore, be low. There was also a marked time effect, so that it is advisable to measure this absorption immediately after the solution has been reduced.

(6) Filtration of Solution

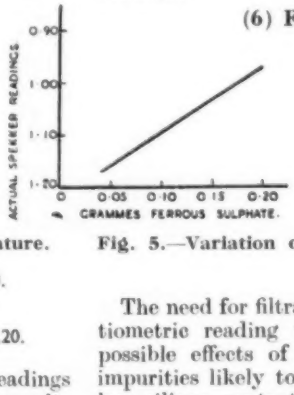


Fig. 5.—Variation of absorption with ferrous sulphate addition.
Spekker Details.
0.50g Sample.
0.30% Chromium.
Filters = Ilford 601 + H503.
Lamp = Mercury Vapour.
Cells = 2Cm.
Water : Water Setting 1.20.
Temperature = 20 °C.

The need for filtration of the solution prior to absorptiometric reading was considered in relation to the possible effects of high silicon contents or of other impurities likely to yield insoluble precipitates. With low silicon contents, e.g., 0·1 to 0·2%, the possible effect was considered to be negligible but with higher silicon contents, turbidities would be noticeable and may, depending on the technique, have a positive effect on the chromium values obtained. For example, if absorptiometric readings are taken of the same portion of solution, first in the oxidised state and then in the reduced state after adding ferrous sulphate to the cell, the effect of the turbidity may well, within limits, be eliminated. This practice is not recommended in routine batch determinations on account of the possibility of contaminating the subsequent oxidised test solutions with unremoved traces of the reducing agent. In routine batch determinations, the preferred practice is to measure first the absorption of all the coloured

solutions, reduce the remaining unused solution with ferrous sulphate and again measure the absorptions for all the reduced solutions.

This practice necessitates that the second absorption reading (i.e., the reduced solution) is obtained on a different portion of the original solution, so that a variation in the amount of turbidity would affect the reading obtained. In extreme cases, therefore, the removal of any precipitate from the original coloured solution before measurement would appear to be desirable.

Tests were carried out, therefore, on a number of low silicon steels in order primarily to ascertain whether the filtering operation would seriously modify the intensity of the colouration, if an occasion arose when removal of an excessive silicic acid precipitate was deemed necessary. In these tests, two modifications were compared with the results obtained on the unfiltered solution :—

(*a*) Filtration through Whatman No. 541 papers.

(*b*) Filtration through sintered glass crucibles.

The results obtained are shown in Table VI, in which the absorptiometric readings have been converted into chromium per cent. using a calibration curve prepared from synthetic solutions which were substantially free from precipitated silicic acid.

TABLE VI.—THE EFFECT OF FILTRATION ON THE CHROMIUM CONTENT OF LOW SILICON STEELS (Si 0·10%).

Steel	Accepted Chromium Value	Method of Filtration		
		Filter Paper	Sintered Glass Crucible	Unfiltered
A ..	0·27	0·235, 0·255, 0·235	0·265	0·255, 0·255
B ..	0·16	0·135, 0·135, 0·135	0·16	0·16, 0·155
C ..	0·09	0·08, 0·085, 0·085 0·075	0·09	0·09, 0·09
D ..	0·03	—	—	0·03, 0·03
E ..	0·065	—	0·075	0·07, 0·07, 0·065, 0·065
F ..	0·185	—	0·185, 0·19	0·185, 0·185, 0·19, 0·19
G ..	0·185	—	0·19	—
H ..	0·30	0·275, 0·275	0·30, 0·295	0·30, 0·30

The results indicate that removal of precipitated silicic acid by filter papers is not to be recommended ; low results are obtained, particularly with the higher chromium contents, which suggests that the filter paper exerts a measurable degree of reduction of dichromate. The results obtained after filtration through sintered glass filters agree closely with the accepted values and with those obtained on the unfiltered solutions. It is clear, therefore, that with steel of low silicon content, filtration is unnecessary and that when filtration is unavoidable, a sintered glass filter should be used. It is possible that the slight effect due to filtration through a filter could be compensated by relating the absorption readings to a calibration curve prepared from similarly filtered solutions, but such a procedure would be unwise as the degree of reduction will doubtless vary according to the conditions of filtration, e.g., paper, time, temperature, etc.

TABLE VII.—RESULTS OBTAINED ON A SELECTION OF CARBON AND LOW ALLOYED STEELS.

Steel	Type	Accepted Chromium Value %	Percentage Chromium by the Perchloric Acid Method
ASC 138 ..	—	0·08	0·075 0·075
ASC 139 ..	—	0·11	0·105 0·11
ASC 140 ..	—	0·07	0·065 0·065
504	0·7 C, 0·4 Mn, 0·1 Ni	0·06	0·06 0·065 0·07 0·06
4453.. ..	0·8 C, 0·7 Mn, 0·1 Ni	0·08	0·075 0·075 0·08 0·085
3112.. ..	0·7 C, 0·8 Mn, 0·2 Ni	0·14	0·13 0·135 0·14

General Application of the Method

Having regard to the limitations, as revealed by the results of the foregoing experiments, the method (details of which are given in Appendix II) has been applied to a large number of carbon and low alloyed steels and a selection of typical results is given in Table VII. It will be seen that the results indicate a high degree of reproducibility and show good agreement with the accepted chromium contents of these steels.

The method as described in Appendix II is simple and very speedy. Attention may well be drawn to a few features.

Satisfactory results are obtained in the use of the Spekker Absorptiometer with either the mercury vapour or tungsten filament illuminations. With the former, Chance No. 6 filter with Wratten No. 50, or Ilford 601 with H.503 filters are suitable, whilst with the tungsten filament lamp, Ilford 601 filter is to be preferred.

The use of 0·5g. or 1·0g. sample weights is largely a matter of individual preference. While slightly beneficial effects may be derived in certain cases from the smaller sample weight, it must be remembered that the absorption value of the coloured solution is reduced to approximately a quarter when a 0·5g. sample is used in place of a 1g. sample. For low chromium contents, this will greatly reduce the accuracy of measurement.

The size of cell employed depends also on the sample weight and on the chromium content. Suitable combinations are given in Note 3 of Appendix II.

Summary and Conclusions

Based on the colour intensity of dichromate in perchloric acid solutions containing ferric iron, a colorimetric method for low contents of chromium in steel has been critically examined. Although the method is very simple and speedy, several factors have been shown to exert a marked effect on the colour intensity of the solution. These factors include the perchloric acid concentration, iron concentration, presence of alloying elements, temperature and effect of filtration.

With carbon steels of known general composition, the method offers distinct advantages in its simplicity, speed and reproducibility. With other materials, which may contain alloying elements, the method suffers from certain limitations, due largely to the effect of replacing iron by the alloying elements, rather than to the alloy itself. Of the common alloying elements, only molybdenum and vanadium in large amounts interfere, but in small (i.e., 1·0%) amounts, their effect may be neglected. Careful adherence to the specified conditions is also essential for satisfactory operation.

In view of the foregoing, it has been decided that this method is hardly suitable for submission as a Standard method. The obvious advantages of the method under routine conditions are manifest provided the limitations are fully appreciated.

APPENDIX I

Method published by L. Singer and W. A. Chambers*

Procedure

Preparation of Solution.—Transfer 1·000 gram. of sample for steel containing up to 0·1 chromium, to a 125 ml. Philips beaker and dissolve in 10 ml. of dilute nitric acid (1 to 1) and 20 ml. of perchloric acid (70 to

(*Industrial and Engineering Chemistry, Analytical Edition*, August, 1944, p. 507)

72%). For steel containing between 0·1 and 1% of Chromium take a 0·500-gram sample and dissolve in 10 ml. of nitric acid (1 to 1) and 15 ml. of perchloric acid (70 to 72%). Evaporate to dense fumes of perchloric acid and boil gently for five minutes to oxidise chromium (boiling for 8 minutes does no harm). Cool the beaker and contents rapidly in water. Dissolve soluble salts with 20 ml. of water and transfer the solution to a 50-ml. glass-stoppered volumetric flask. Cool the solution to room temperature and dilute to 50 ml.

Taking the Colorimeter Reading.—Transfer a portion of the solution to the absorption tube and reduce with a small crystal (about 10 to 20 mg.) of ferrous ammonium sulphate. Adjust the colorimeter so that the reading on this solution is zero. Discard the solution in the absorption tube, refill with oxidised solution, and take a second reading. This reading is a measure of the colour due to the dichromate. In the absence of elements which form highly coloured ions, such as copper, nickel, cobalt, etc., it is not necessary to reset the colorimeter at zero. All subsequent colorimeter measurements are made by taking a reading on an oxidised solution, reducing the solution in the absorption tube with a small crystal of ferrous ammonium sulphate, and taking a second reading. The difference between the first and second reading then represents the colour due to the dichromate present. If appreciable amounts of highly coloured ions are present, the colorimeter is adjusted to read zero on the reduced solution before a reading is taken on the oxidised sample.

APPENDIX II

Absorptiometric Determination of Residual Chromium in Carbon and Low Alloyed Steels by the Perchloric Acid Method.

Dissolve 1g. of sample in 10 ml. nitric acid (1 : 1) and 23 ml. perchloric acid (sp. gr. 1·54) contained in a covered 200-ml. conical beaker (Note 1). Evaporate the solution to fumes of perchloric acid and boil gently for five minutes whilst still fuming. Cool rapidly, add 20 ml. distilled water to dissolve the separated salts, and cool again (Note 2).

Transfer to a 50-ml. graduated flask, and dilute exactly to 50 ml. Mix the solution thoroughly and measure the absorption by means of the Spekker Photo-Electric Absorptiometer (Note 3).

Add 0·02–0·04g. of ferrous sulphate crystals to reduce the chromium, and again measure the light absorption (Note 4). To obtain the chromium content, relate the difference between the drum readings to a standard calibration curve prepared from known tests treated as above.

NOTE 1.—With 0·50g. samples use 18 ml. perchloric acid (sp. gr. 1·54).

NOTE 2.—With silicon contents less than 0·10% filtration is unnecessary, but with larger amounts it may be necessary, depending upon the technique employed for the reduction with ferrous sulphate. Where filtration is unavoidable, sintered glass crucibles should be used.

NOTE 3.—*Size of Cell.*—The size of cell to be employed depends upon the weight of sample taken and the chromium content of the steel.

1·0g. *Sample.*—For chromium contents less than 0·15% use 2 cm. cells ; for chromium contents between 0·15 and 0·35% use 1 cm. cells.

0·50g. *Sample.*—For chromium contents less than 0·10% use 4 cm. cells ; for chromium contents between 0·10 and 0·40% use 2 cm. cells.

Filters.—With the Mercury Vapour lamp use either Chance No. 6 and Wratton No. 50 filters or Ilford 601 and H.503 filters. With the Tungsten Filament Lamp use Ilford 601 and H.503 filters.

NOTE 4.—The same solution can be reduced in the cell, or else the whole of the remaining solution in the beaker can be reduced, and the absorption measured on a fresh portion. The readings should be taken immediately after reduction has occurred. The amount of ferrous-sulphate specified, i.e., 0·02–0·04g. is sufficient to reduce the total amount of oxidised chromium present in the 50 ml. of solution.

Correspondence (*Continued from page* 219)

too cautious. I will try to clarify my views by saying that I think zinc, aluminium, lead and tin should be cleaned with trisodium phosphate, etc., with a free rinsing soap, where this is not harmful, and a pH range from 8–10·5. The electro-plater cleaners and light-duty cleaners need a pH range from 10–12·5, while cleaners for a harder service (caustic soda) require from 12–13·5. Lead, zinc, and tin are, or should be, cathodically cleaned, but steel can be cleaned either anodically or cathodically. There is always, however, a danger of hydrogen embrittlement and smut. Anodic cleaning is better *when it can be used*. Alkalis tend to form an absorbed film on the surface of metals, and therefore it is often advantageous—especially if the cleaning comes before plating—to follow up with a hot-water spray and then swill in a dilute solution of an acid tartrate, or, for steel, acid phosphate—e.g., potassium. I am not so convinced as Mr. Liddiard that a soap is inadvisable in all alkaline cleaning, and many production engineers not only continue to use them, but regard them as indispensable for those classes of work in which the material to be removed consists of vegetable or animal fats or fatty acids. I agree, however, that their importance has been overestimated.

With the other points in Mr. Liddiard's letter, I have no quarrel.

Yours sincerely,
R. GROVES.

A Non-Ferrous Merger

NEWS of an interesting amalgamation in the field of non-ferrous foundry and engineering work has reached us. The two old-established Stoke-on-Trent firms of T. M. Birkett & Sons, Ltd., of Hanley, and Billington and Newton of Longport, have decided to join forces and pool their resources and technical experience. That this will be to the advantage of the customers of both firms is clear, since the activities of the two firms have been on parallel rather than identical lines. While Messrs. Birkett have concentrated on intricate small and medium work, the foundry of Messrs. Billington and Newton is specially equipped for the production of the largest type of non-ferrous castings. It is noteworthy that Messrs. Birkett's supplied the phosphor-bronze bars from which the bushes for the "Flying Wing" jet plane were made.

The Cleaning of Metals

Part IV—Emulsifiable Cleaners

By R. Groves

Emulsifiable cleaners do not corrode or tarnish the majority of materials and have a wide range of application. The work for which they are particularly advantageous is described and some of their drawbacks are referred to. Care in the choice of washing machines is emphasised and some of the factors which determine the choice are discussed.

IN using cleaning materials of the petroleum spirit type, all apparatus must be properly earthed to prevent sparks from static electricity. The tanks must be provided with covers that close automatically and have fusible controls, while electric motors operating in conjunction with the cleaning process must be proofed against explosion, as must the wiring. Ventilating arrangements must be given special attention, and the dampers used should be of sound design, while safety doors are essential. In addition to all this, there should be an automatic sprinkler or other system installed capable of immediate operation the moment a fire breaks out, and adequate to ensure its complete extinction. The normal device is a series of carbon dioxide vessels efficiently connected to an automatic arrangement that blankets with a vapour preventing all combustion the area in which a fire has begun.

Cleaning with these distillates presents no difficulty other than that of fire prevention. The parts to be cleaned are immersed in, or sprayed with, the spirits drained, and dried by an air blast or by air provided by a blowing engine. Their use is, however, strictly limited to the functions described in the previous article.

Emulsifiable Cleaning Materials

These cleaners are relatively inexpensive, do not corrode or tarnish the majority of materials, and have a wide range of application. They are based on a penetrating and dispersing agent capable of being dissolved in oil. The agent is compounded with paraffin or a safety solvent in the ratio of 1 : 10. This solution is usually sprayed on to the parts to be cleaned or may be used in tanks, the parts being dipped in it. About half a minute is usually enough to carry out the cleaning operation, which is followed by rinsing in a spray of cold water to remove all traces of the dirt-carrying solution. The solution actually forms an emulsion with the water, and the particles of dirt are carried in suspension in this emulsion. After washing, the surface is left extremely clean, though there may be a slight quantity of the solvent left on. This, however, whether paraffin or some safety solvent, quickly evaporates, and for painting, lacquering, and many other later operations is quite harmless.

Application of the Emulsifiable Cleaners

The solution itself has no corrosive action and does not ignite until its flash-point is reached. As it is usually employed at normal temperature, its use presents, therefore, little risk. The surface produced is *physically*, as distinct from chemically, clean, and as such is superior to that left by the solvent degreasing agent, since there is no need for hand-wiping or alkaline solutions afterwards, except, of course, where plating or vitreous enamelling are called for. Emulsifiable cleaners are particularly advantageous as a means of cleaning parts for bonderizing, the reason being that the surface is not passivated.

This type of cleaner can be applied to those parts that are not suitable for the degreaser solvent, and where a cleaner surface than degreasing provides is required. It can be used when alkaline solutions fail to eliminate particularly stubborn dirt. As stated, it is mostly used at room temperature, or barely warm, so that the cost of heating is largely avoided, unless the rinsing is carried out with hot water to accelerate the drying of the finished parts.

These cleaners have, in short, many of the good points of both alkaline and solvent degreaser cleaning agents. They are specially suitable for eliminating carbon dirt from steel, and for this work excel the other cleaners. Where the cost of hand-wiping or brushing has to be avoided, they can be successfully used for cleaning polished, buffed, heavily oiled, drawn and stamped parts, as well as parts that have been lubricated in machining.

Drawbacks of the Emulsifiable Cleaner

On the other hand, certain parts cannot be effectively dealt with by this type of cleaner. Examples are parts that nest or lock together, so producing recesses that are difficult to drain or that cannot be reached by the sprays in rinsing. Parts that have deep recesses should also not be cleaned by these agents unless the washing machine is so designed that thorough draining and full efficiency of the spray are mechanically achieved. Hence, great care must be paid to the correct choice of machine.

The Washing Machine

It now becomes necessary to consider the machine in relation to the parts to be cleaned and the type of cleaning material used. A washing machine for the cleaning of metals is essentially a complete unit by whose means the work is carried out either fully automatically or semi-automatically. This does not mean that every cleaning operation calls for a washing machine, though even when no machine is used it may be necessary to install some form of handling appliance to deal with the parts. In this article the word "machine" will be taken to include every form of washing appliance from the plain bath or tank to more complex apparatus.

The main points to be borne in mind in choosing the machine are: (*a*) The form of the parts; (*b*) their dimensions; (*c*) the extent to which they are liable to suffer damage if carelessly handled.

(*a*) is specially important, because complicated parts having deep pockets or depressions may present serious problems both in cleaning and in draining and rinsing.

Sometimes the form may be such that parts will be liable to interlock when jumbled together in work baskets or other holding means, and so form blind holes. If the parts are easily notched, grooved, or distorted, it may be impracticable to use methods of handling that would be quite satisfactory with less readily indented or distorted parts. This is particularly so when the parts are hollow or deeply pocketed.

Influence of Size

(*b*) is also important because it affects the method of handling. Small pieces are nearly always dealt with in mass, either in work baskets or on trays, according to their form and liability to damage. Parts of medium size can be handled singly on conveyors of flat or chain type, or may even be given special holding means if liable to damage. Large parts are always dealt with singly and conveyed as above, though overhead conveying is often used, as are rotating tables. Where the parts are readily injured, they are usually enclosed in suitable containers so as to prevent their knocking up against each other. Parts of unusually large size are normally moved by special conveyors or platforms.

(*c*) Hollow or deeply recessed parts are liable to interlock when dealt with in mass, so that they cannot be cleaned in barrel-type containers, which are rotated. Great care must be taken to ensure that they are reached in every nook and crevice by the cleaner and properly drained. If cleaned individually, they are normally held in a vertical position with the aperture or recess down. If treated in mass, they have to be revolved, or washing and draining may be incomplete.

Assuming that a considerable number of parts have to be cleaned, and that these represent a large bulk, the choice of machine is determined by the means adopted for moving the parts—i.e., on the type of conveying apparatus adequate to the form, dimensions and liability to injury of the parts. Where only a small number of pieces have to be treated, a plain tank will suffice combined with some means of heating, for small and medium-sized parts. Larger pieces can be cleaned in bigger tanks, heated, and furnished with overhead hoisting or lifting appliances, again assuming only a small number of parts are required. Extremely large parts can be sprayed and rinsed under pressure in compartments adapted for the work, or in a corner of a workshop provided with suitable draining means. This, again, applies only to small quantities.

Influence of Quantity

The number of parts per hour is the standard to be adopted in determining the influence of quantity on choice of machine. In general, flat conveyor machines yield a production in strict ratio to the width of the belt and the speed at which it is run. Barrel type machines yield a production directly governed by the pitch of the worm wheel and the number of revs. per minute.

Parts to be cleaned may be finished wet, dry, hot or cold, and this governs the provision of drying or cooling means in the machine, or possibly both, since both conditions may on occasion be required. If the part has a considerable surface area, being of large size, it may dry itself out if rinsed in hot water after cleaning with a hot solution. In such instances it will not be necessary to include a mechanical dryer in the machine, but as against this a cooling mechanism might be necessary because otherwise the parts would probably be too hot for handling. Parts of slight cross-section may cool before they have dried out, which necessitates provision for mechanical drying in the machine, but then no mechanical cooling is needed.

Some machines embody in their construction the means not only of washing, rinsing, and drying or cooling the parts, but also of carrying out other finishing processes, such as pickling, ball burnishing, painting, bonderizing, and even a number of plating operations.

Methods of Heating

Only the emulsifiable cleaners are used cold, or nearly so; all other cleaning solutions have to be heated. The heating is accomplished by steam coils or immersion gas burners, though in America it is often found more economical to employ oil immersion burners. Immersion electric heaters are also used in some parts where electric current is relatively cheap.

The room available in the plant for the washing machine may have an influence on the type chosen. It may, for example, be necessary to plan operations in vertical rather than horizontal progression where space is extremely restricted. There are other ways in which space can be economised—e.g., by employing double conveyors, which give twice as great a production per unit of floor area.

The link the cleaning process forms with the chain of production must never be overlooked in choosing or ordering a washing machine. The method of handling the parts in the production sequence may not coincide with that provided in a standard suitable machine, which will consequently have to be modified. Loading may take place at one end of the machine and discharge at the other; but in some conditions it may be better to have both loading and discharge at the same end. The machine maker should always be consulted and given a clear picture of the sequence of operations of which cleaning is one.

The Cost Factor

Many economies can be effected in the cleaning process by thought in choosing cleaning agents and machine; the point to be remembered, however, is that the key factor is not the cost of the cleaner per part cleaned, but the comparative cost of cleaning X parts or X sq. ft. In many instances a dear cleaning material is economical in overall expense. A cleaner that acts rapidly saves conveyor length, enables a smaller machine to be used, and consumes less heat, power, and room. Similarly, a dear washing machine in first cost may prove economical. Again, there are occasions when the best cleaner from the point of view of results may call for serious modification of the existing machine, or necessitate the purchase of a specially designed machine, and so prove dearer in the long run than a slightly less efficient cleaner that could be used with a standard machine or one that needed only slight modification.

Types of Washing Machines

Before considering the various types of washing machines used in cleaning metals, it is necessary to stress that the degree of cleanness required may greatly affect choice of machine. Some parts are cleaned fairly easily but the surface has to be so clean that two washings are essential. Otherwise, a single wash would do. To ensure chemical cleanness, three or even four operations may be necessary. The cleaning agent has an important

influence on choice of machine. Thus, emulsifiable cleaners cannot often be employed for parts that are deeply recessed or hollow when spraying is required, though they might serve quite well if parts are dipped.

There are no cleaning machines that are capable of dealing with every operation. The majority of the automatic machines are constructed to deal with particular difficulties at a particular works, and sometimes for a particular operation only at the one works. Nevertheless, there are certain basic principles common to all mechanical washing machines and a summary of these will assist the reader in his choice. It should be noted that because a certain apparatus has solved a particular cleaning problem, it does not follow that that machine will solve the problem at a different works, which has its own methods, peculiarities and conditions. Modifications may be needed to ensure success.

In the next article, the simplest forms of cleaning apparatus will be dealt with, after which the mechanical machines will be discussed.

Correspondence

The Cleaning of Metals

The Editor, METALLURGIA,
Dear Sir,

The articles by Mr. R. Groves on the cleaning of metals which are now appearing in METALLURGIA do call for some comment, since a number of statements included in the articles are inclined to be somewhat misleading.

I feel that Mr. Groves, in setting out to write a useful and practical article on "The Cleaning of Metals" without referring to any proprietary cleaners by name, or even of particular chemical compounds or mixtures, is setting himself an impossible task. Advice on concentrations and temperatures and such like must necessarily be of little value unless we can be told what alkaline proprietary cleaner or specific chemical mixture the author has in mind. He seems to realise this himself when he advises us to put our particular problem before a reputable maker of cleaning materials and get advice and samples from him. That, if I may say so, is good advice and that most of us already do.

Mr. Groves is also rather misleading in his reference to the use of alkaline cleaners for aluminium, brass, tin, zinc and copper. At one moment we are told that we must on no account use alkaline materials to clean these metals. In the same paragraph we are later told that for these metals it is *sometimes*, if not always, necessary to use a non-alkaline cleaner. In the next paragraph we are instructed to use alkaline cleaners when articles are to be electro-plated. The fact is, of course, that one can, and should, use alkaline cleaners for some if not all of these metals for certain purposes, but when this is done special precautions must be taken to avoid these troubles of staining, corrosion, etc., to which the author refers.

Among the treatments which require an alkaline process prior to the treatment are chromate protection of tinplate, phosphate treatment of steel and zinc, such as Walterising, Parkerising, etc., anodising of aluminium and electro-plating of all metals. All of these metals and alloys can be, and are frequently degreased in alkaline solutions nowadays. More is known of the mechanism of the corrosion and discolouration in alkaline solutions and steps can be taken to prevent this. Thus some years ago it was found that tin plate was not stained by alkaline solutions alone, but by the presence of oxygen in the solution[1] and steps could be taken to remove this by simple reduction. The presence of a reducing agent such as sodium sulphite[2] was found to be a satisfactory means for preventing typical spangling and feathering which can occur on tinplate if these precautions are not taken. Alternatively it may be necessary to prevent the development of oxygen at the metal surface which can result from the setting up of a bimetallic cell within the degreasing solution.[3]

Copper is discoloured in the same way by oxidation, more particularly in drying from alkaline solutions, but again, the presence of reducing agents can prevent this. Large numbers of copper articles are degreased in strong alkaline solutions electrolytically using the hydrogen produced as a reducing agent; in other words, making the work cathodic. Copper alloys are more difficult since bimetallic cells are set up between the alloy phases with the cleaner as the electrolyte.

With brass, for example, this can be overcome by the presence of an alkali-stable reducing agent, degreasing cathodically, or by incorporating siliceous alkaline silicates in the degreasing solutions which increase the viscosity slightly and also "plate" silicate ions cataphoretically on the more electro-positive phase in this way preventing oxygen formation. These films are later rinsed away leaving the bright surface.

Aluminium is often degreased in the presence of silicates which prevent the formation of soluble sodium aluminate by combination with the surface of the metal to give insoluble silicates.

The author's references to the use of soaps are somewhat vague. The modern tendency is to avoid their use entirely in alkaline degreasing, since they readily hydrolyze and can easily film up the anodes in electrolytic solutions. In degreasing solutions to be sprayed the presence of soaps in quantities of sufficient surface activity means excessive foaming, and this is an annoying feature. Synthetic surface active agents chosen for specific properties are far more satisfactory both for initial wetting and emulsification and such materials are available nowadays with a low foam stability.

Yours faithfully,
For The Glacier Metal Co., Ltd.
(signed) P. D. LIDDIARD,
Chief Metallurgist.

The Editor, METALLURGIA.
Dear Sir,

Naturally, I avoided mentioning the names of proprietary cleaners, as I do not think a general article of this type should be veiled advertisement. As a mild alkaline cleaner, I have found sodium metasilicate effective. Sodium tetraborate and sodium orthosilicate are also useful according to the pH level required, but there are so many factors involved that it is impracticable to make dogmatic recommendations without knowing the particular problem.

If my remarks on alkaline cleaners were misleading, I am sorry, but, as Mr. Liddiard points out, there are so many limitations on the use of these cleaners that in trying to avoid dogmatism I perhaps became somewhat

(*Continued on page* 216)

1 *J. Soc. Chem. Ind.*, 1935, **54**, 217–221.
2 *B.P.*, 451,025.
3 *B.P.* 528,683.

MICROANALYSIS

CHEMICAL AND PHYSICAL METHODS

APPARATUS METALLURGICAL APPLICATIONS

THERE is much to commend the recent practice, in Analytical Chemistry, of inviting chemists prominent both in industry and in the academic side, to put forward for discussion their ideas about the present position of analytical chemistry, its practice, and the methods used in teaching it. Some repetition of ideas must of necessity be found. Not infrequently we find ourselves in various stage of disagreement, from the mild to the violent, with what the writers have to propound. But most often we find ourselves either strongly in agreement, or even envious of conditions shown to be in existence in the United States of America. Such a series of articles, no matter how controversial they may be, can do nothing but good to the position of analytical chemistry in that country. Indeed, it might be truer to say that the more controversial the articles may be, the more good they are likely to do. If everything that had to be said were a glowing testimonial, then undoubtedly the reader would become suspicious of a state of affairs smacking of "the best of all possible worlds." The articles show, however, that much remains to be done in order to bring analytical chemistry up to the level which its practitioners would wish for it. They show also, that there are people, eminent in their various spheres, who are both well aware of this, and fully determined to do something about it. In this country, we have, in the first place, no such ready platform offered to us. If we had, one wonders whether we would have the people who could and would discuss, soberly and frankly, the problems of analytical chemistry. We ourselves would like to think that it is only the opportunity for discussion that is lacking, and not the urge. But we cannot, equally, help feeling that if the urge existed, the opportunity would be made.

The Microchemical Aspects of the "Dead-Stop" End-Point Titration Method

By J. T. Stock

(L.C.C. Norwood Tech. Inst., Knight's Hill, West Norwood, London, S.E. 27).

Although the "dead-stop" end-point titration method has, in the past, been applied primarily to the determination of small amounts of substance present in low concentration in large bulks of solution, there is nothing inherent in the method which would prevent its application on the drop-scale. Apparatus suitable for this type of determination is described, and typical estimations are discussed.

THE term "determination of small quantities" may imply small samples, low concentrations, or both. Many electrochemical methods, such as electrodeposition,[1] polarography,[2] amperometric titration[3] and techniques such as pH measurement[4] or potentiometric titration[5, 6, 7] have been employed in the examination of small samples as well as in cases of low concentration of the substance to be determined. The "dead-stop end-point" method[8] has, on the other hand, been restricted mainly to applications involving low concentrations of a substance in a sample of macro-size. Since, however, (i) the essential polarisation phenomena occur at the electrode surfaces and not in the bulk of the solution and (ii) minute changes in electrical energy may be readily detected, using, if necessary, modern electronic devices, there seems to be no reason why titration on the drop scale, with electrodes of appropriate size, should not be possible.

1 Sand, H. J. S., *Electrochemistry and Electrochemical Analysis*, Blackie, London, 1940, Vol. II, p. 123; *idem*, *Metallurgia*, 1944, **30**, 107; Fife, J. G., *ibid*, 1944, **30**, 167.
2 Stock, J. T., *Metallurgia*, 1944, **29**, 155.
3 Stock, J. T., and Fil, M. A., *ibid*, **37**, 221; 1947, **36**, 51; *ibid*, **30**, 277.
4 Stock, J. T., and Fil, M. A. *ibid*, 1946, **33**, 219, 271.
5 Furman, N. H., *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 213; 1942, **14**, 367.
6 Ashcraft, E. B., *Trans. Amer. Electrochem. Soc.*, 1940, **78**, 127.
7 Stock, J. T., *Analyst*, in the press.
8 Foulk, C. W., and Bawden, A. T., *J. Amer. Chem. Soc.*, 1926, **48**, 2,045.

General Principles

When a small e.m.f. is applied to a pair of unattackable electrodes dipping into a solution containing no depolarising substances, little or no current flows. This is due to the formation of thin layers of hydrogen and oxygen upon the cathode and anode respectively. The electrodes are thus *polarised* and current cannot flow unless the depolarisation of *both* is effected. In the "dead-stop end-point" method of titration, the conditions are usually arranged so that the solution to be titrated contains a substance which is able to destroy the polarisation either of the cathode or the anode. Thus, in the determination of sodium thiosulphate by titration with iodine solution, the thiosulphate acts as an anode depolariser:

$$2\,S_2O_3^{--} + H_2O + O = S_4O_6^{--} + 2\,OH^-$$

Since the sodium ion cannot act as a cathode depolariser under the conditions appertaining, the cathode remains polarised and current does not flow.

On titrating with iodine solution in the usual manner, the iodine is converted into iodide, which can also act as an anode depolariser. Immediately after passing the end-point, however, free iodine persists in the solution. Iodine (but not iodide) acts as a cathode depolariser:

$$I_2 + 2H = 2H^+ + 2I^-$$

Since the anode has been maintained in the depolarised state, originally by thiosulphate, finally by iodide ions, current now commences to flow. The end point of the titration is thus indicated by the sudden commencement of current flow through the solution.

Owing to momentary production of high local concentrations, each addition of reagent may cause the galvanometer spot or pointer to make a temporary excursion from its zero position. This effect, which depends upon the rate of titration, efficacy of stirring and proximity to the end-point, is due to partial depolarisation of the cathode, and its magnitude often affords useful warning of the approach of the end-point.

It is obvious that if conditions are adjusted so that depolarisers of both electrodes are initially present and that the removal of one or both of the depolarisers coincides with the end-point, then a reverse effect—viz, an initial flow of current falling abruptly to zero at the end-point, will be obtained.

Apparatus

As shown in Fig. 1, the electrode system and ancilliary electrical apparatus may be very simple. Electrodes AA consist of short lengths of stout platinum wire sealed through the closed ends of lengths of 6-mm. diameter glass tubing. Electrical connections are made by copper wires dipping into a drop of mercury in contact with the inner ends of the platinum electrodes. Alternatively, a 15-cm. length of platinum wire may be sealed in so that the short projecting piece serves as the electrode. The other end emerges from the end of the supporting tube, thus allowing direct attachment to the copper connecting wire.[9] Various

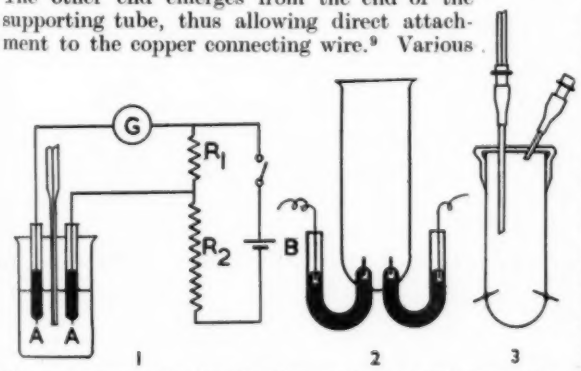


Fig. 1.—Apparatus for titration by the "dead-stop end-point" method.
Fig. 2.—Titration cell with sealed-in electrodes.
Fig. 3.—Titration cell for use with hypodermic-type micro-burette.

modifications in design may be made; thus the platinum wire electrode may be formed into a spiral or into a loop[10, 15], or may be replaced by a rectangle of platinum foil.[11] The electrodes may be sealed through the walls of the titration vessel, an arrangement of obvious utility for handling small volumes of solution such as might be encountered in microchemical analysis. A titration vessel of the type shown in Fig. 2, although designed originally for conductometric titration[12] is useful in this respect. A sealed-in electrode system is also useful when, in order to avoid interference by extraneous moisture, a closed titration vessel has to be used. In the design shown in Fig. 3, the vessel and its electrodes may be thoroughly dried out in an oven and then stored in a desiccator until required.[13] Having introduced the sample, the vessel is closed by a rubber serum bottle cap, which has been dried and stored in the same manner. The jet of the microburette is a hypodermic needle, which is forced through the diaphragm of the cap when required. A second, finer hypodermic needle is also inserted to act as an air vent. When the needles are withdrawn, the punctures close up and the vessel may then be shaken without loss of contents. Agitation of the solution during titration is effected by gently tapping the cell; in most other forms of apparatus, agitation is usually effected by a small glass stirrer which is driven either electrically or mechanically.

The desired e.m.f. is applied to the electrodes by means of the potentiometer system shown in Fig. 1. This consists of two fixed resistors R_1 and R_2 which are energised by cell B. The latter may be a 2-volt accumulator or a single dry cell. The total resistance of R_1 and R_2 is about 1,000 ohms and their ratio is such that an e.m.f. of from 10–20 millivolts is applied to the electrodes (higher e.m.f's. are sometimes recommended[14, 15]. If desired, R_1 and R_2 may be replaced by a single resistor which is provided with a sliding contact, such as, for example, a radio-type potentiometer. Any e.m.f. up to the full voltage of cell B may then be applied to the electrodes.

A galvanometer G, of sensitivity from 50–200 mm. per microampere, is used to detect the end-point. Since the instrument is used only as an indicator, no calibration is necessary. To avoid damage, it is advisable to provide the galvanometer with an adjustable shunt, thus enabling its sensitivity to be reduced when conditions likely to cause a large flow of current are encountered.

Electronic Devices

Detecting devices incorporating thermionic valves may also be used. The circuit shown in Fig. 4 is a comparatively early example of this technique.[16] The e.m.f. applied to the electrodes is adjusted by potentiometer P and by shunt resistor R_1. Having placed the electrodes in the solution, resistor R_2 is adjusted until galvanometer G reads zero and the titration is commenced. The change in polarisation phenomena occurring in the region of the end-point alters the potential difference between the electrodes, and hence the potential impressed upon the grid of the valve. A relatively large change in the anode current of the valve is thus produced, causing the system to become unbalanced and the galvanometer to register a deflection.

Electronic technique also allows the usual mirror galvanometer to be dispensed with, the apparatus thus being rendered much more compact and portable. A "magic eye" radio tuning indicator, which may be

9 Bishop, R. L., and Wallace, E. L., *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 563.
10 Wernimont, G., and Hopkinson, F. J., *ibid*, 1940, **12**, 308.
11 Hewson, G. W., and Rees, R. L., *J.S.C.I.*, 1935, **54**, 254T.
12 Callan, T., and Horrabin, S., *ibid*, 1928, **47**, 329T.
13 Levy, G. B., Murtaugh, J. J., and Rosenblatt, M., *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 193.
14 Sillars, I. M., and Silver, R. S., *J.S.C.I.*, 1944, **63**, 177.
15 Carter, R. J., and Williamson, L. J., *Analyst*, 1945, **70**, 369.
16 Kassner, J. L., Hunze, R. B., and Chatfield, J. N., *J. Amer. Chem. Soc.*, 1932, **54**, 2,278.

readily mounted on the burette stand immediately in front of the operator, is used. By suitable adjustment, the area of fluorescence on the screen of the indicator may be made to shrink to a minimum at the end-point. The circuit depicted in Fig. 5 employs this form of indication,[17] and is a modification of a titrimeter described earlier by Serfass.[18] A similar arrangement, claimed to eliminate fuzziness and flickering of the image has recently been described.[19] Titration apparatus using the "magic eye" as an end-point indicator is available commercially.[20]

Applications

Following the original work of Foulk and Bawden,[8] most of the titration processes to which the method has been applied are iodometric ones. Owing to its importance in technical analysis, the determination of water by use of the Karl Fischer reagent[21] has been the subject of much study. The end-point may be detected potentiometrically using a platinum-tungsten electrode pair,[22] but the e.m.f. jump at the end-point is small and time for re-establishment of equilibrium after each addition of reagent must be allowed. Wernimont and Hopkinson[23] showed that the application of the "dead-stop end-point" method simplified the procedure, and these workers applied the technique to the determination of quantities of from 4–200 milligrams of water in methyl alcohol, acetone, etc.

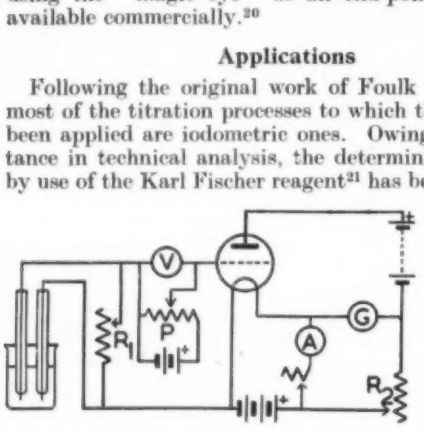


Fig. 4.—Thermionic device for end-point detection.

Many workers recommend addition of an excess of the Karl Fischer reagent to the sample, followed by back titration with a standard solution of water in methyl alcohol. However, others, [15, 24] found direct titration to be satisfactory in the determination of water in synthetic resin solutions, oils, etc. A study of the polarisation phenomena occurring during the direct titration has been made by Carter.[25]

Using an electronic indicator and the cell shown in Fig. 3, Levy and his co-workers have shown that quantities of water of from 1–25 milligrams may be determined with a precision of from 20–100 micrograms.[13] An ingenious method was used to permit the determination of water in pencillin sodium salt which was packed in small, rubber-capped bottles. Two hypodermic needles were thrust through the stopper and a 7·5-cm. length of 30-gauge platinum wire was slipped through each needle, so that when the needles were withdrawn the rubber closed on the wires. The lower ends of the wires acted as electrodes, and, after completing electrical connections, titration from a burette fitted with a hypodermic needle jet could be accomplished without exposing the contents of the bottle to the atmosphere.

Small quantities of water in cereal products,[26] petroleum fractions[27] and in propellant explosives[28] have been determined with the aid of the "dead-stop end-point" method.

In quantitative organic micro-analysis, volumetric methods have been proposed to replace the more usual weighing of absorption tubes. In the case of water, the method depends upon reaction with an easily-hydrolysable acid chloride—e.g., cinnamyl chloride, and the subsequent titration of the hydrogen chloride which is quantitatively liberated.[29] Using the Karl Fischer reagent (which may be used to titrate the water of crystallisation in certain salts[21, 30], it might prove possible to directly titrate the water after its collection in a suitable desiccant which neither interferes in the subsequent titration nor retains the water in a non-available form. (Obviously substances like phosphorus pentoxide, with which water reacts irreversibly, could not be used). Such a procedure would be of value not only in determination of hydrogen, but also in the more uncommon direct determination of oxygen by the hydrogenation technique.[31]

Oxygen in Water

The oxygen content of boiler-feed water is usually determined by the Winkler method, the dissolved oxygen being caused to liberate iodine. Using starch as indicator, the accurate titration of small amounts of iodine is a matter of some difficulty, and may be impossible when feed waters of the very low oxygen content required for high-pressure installations have to be examined. Hewson and Rees[11] showed that the "dead-stop end-point" method could be applied with success and concluded that variations in iodine concentration corresponding to 0·001 ml. of oxygen per litre could be observed.

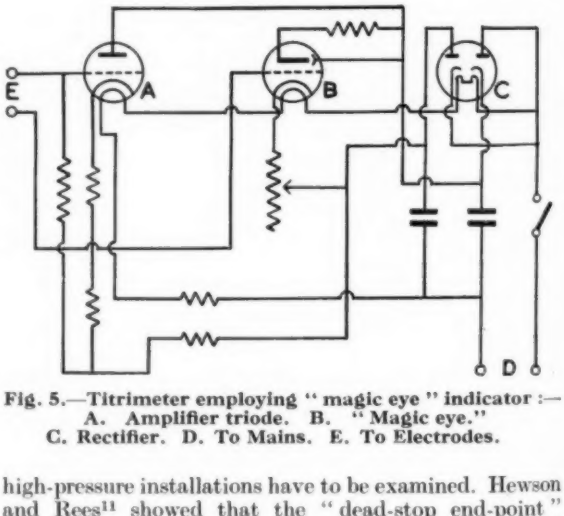


Fig. 5.—Titrimeter employing "magic eye" indicator :—
A. Amplifier triode. B. "Magic eye."
C. Rectifier. D. To Mains. E. To Electrodes.

The accuracy of the method has been further studied; [14, 32] it has been shown that at least 0·2% of potassium iodide is necessary to maintain the depolarisation of

17 McKinney, C. D., Jr., and Hall, R. T., *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 460.
18 Serfass, E. J., *ibid*, 1940, **12**, 536.
19 Kieselbach, R., *ibid*, 1946, **18**, 726.
20 *Mullard—B.T.I. Potentiometric Titration Apparatus*, Baird & Tatlock, Ltd., London.
21 Fischer, K., *Z. angew. Chem.*, 1935, **48**, 394.
22 Almy, E. G., Griffin, W. C., and Wilcox, C. S., *Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 392.
23 Wernimont, G., and Hopkinson, F. J., *ibid*, 1943, **15**, 272.
24 Acker, M. M., and Frediani, H. A., *ibid*, 1945, **17**, 793.
25 Carter, R. J., *Analyst*, 1947, **72**, 94.
26 Fosnot, R. H., and Haman, R. W., *Cereal Chem.*, 1945, **22**, 41.
27 Aepli, O. T., and McCarter, W. S. W., *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 316.
28 Bonner, T. G., *Analyst*, 1946, **71**, 483.
29 Nieuwenberg, van C. J., *Mikrochim. Acta*, 1937, **1**, 71.
30 Mitchell, J., Jr., Smith, D. M., Ashby, E. C., and Bryant, W. M. D., *J. Amer. Chem. Soc.*, 1941, **63**, 2,927.
31 Meulen, ter H., *Rec. trav. chim.*, 1922, **41**, 509.

the anode. Though such an amount is normally present in iodine-thiosulphate titrations involving solutions of normal analytical concentration, the case is otherwise with the 0·002 N solutions used in this class of work. If potassium iodide sufficient to raise the concentration above the minimum figure be added, an accuracy of 0·0005 ml. of oxygen per litre is obtainable.[32, 33]

Ozone, normally present in the atmosphere to the extent of only 10^{-8} by volume, may be determined by its iodine-liberating power. The iodine may be titrated automatically, thus affording a continuous record. Air is drawn continuously through the apparatus in such a manner as to mingle intimately with buffered potassium iodide solution. Small quantities of iodine liberated by the ozone depolarise the cathode of a polarised platinum pair, and the resulting flow of current is amplified until powerful enough to operate a relay which in turn operates an electromagnetically-controlled burette. This delivers a fixed volume (about 0·3 ml.) of 0·0005 N sodium thiosulphate solution, which is injected into the system and destroys the free iodine. As more of the latter is liberated, the cycle of operations is repeated. Each injection of thiosulphate solution is recorded on the clock-driven chart which provides the continuous record.

Other Iodometric Processes

After destruction of organic matter and isolation of selenium by distillation and reduction, very small quantities of this element present in abnormal urines may be determined iodometrically.[10] The precipitated selenium is dissolved in a hydrobromic acid-bromine mixture and treated with sodium sulphite until the colour of bromine is almost discharged. After adding a few drops of phenol solution, 0·001 N sodium thiosulphate solution is run in until an excess of from 2–3 ml. is present and is followed by 1 ml. of 5% potassium iodide solution. Titration with 0·001 N potassium iodate solution to a " dead-stop " end-point is then carried out immediately. In this manner quantities of selenium of from 10–150 micrograms may be determined to within about ± 2 micrograms.

The microdetermination of selenate in the presence of selenite has been studied by Pagel and Miers.[35]

The " dead-stop end-point " technique has also been applied to the determination of copper[36] and of carbon disulphide in carbon tetrachloride.[9] In the latter case, the sample is treated with alcoholic potash ; the xanthate which is formed may, after acidification, then be titrated directly with 0·001 N iodine solution :

$$2\ \ S=C\begin{matrix}OC_2H_5\\ S-K\end{matrix} + I_2 = 2KI + \left[S=C\begin{matrix}OC_2H_5\\ S-\!\!-\end{matrix}\right]_2$$

Since one molecule of carbon disulphide forms one molecule of xanthate, the amount of carbon disulphide may be readily calculated. In the presence of a large excess of carbon tetrachloride, a good end-point cannot be obtained with starch as indicator. Using polarised electrodes, however, samples containing amounts of carbon disulphide ranging from a few parts per million to 200 parts per million could be analysed with an error of about 2%.

Not all workers appear to have met with success in using the " dead-stop end-point " method. Thus it has been reported as proving unsatisfactory in the determination of microgram quantities of iodine.[37]

Determination of Phenols

Of the non-iodometric titration processes which may be followed by means of polarised electrodes, the bromometric determination of phenols in quantities of a few milligrams[38] may be mentioned. The electrodes are immersed in a solution of the phenol in 3 N sulphuric acid which is titrated with 0·1 N bromate-bromide solution from a micro-burette until the presence of free bromine depolarises the cathode. In actual fact, bromine is taken up in stages, at rates depending upon the nature of the substance. Phenol takes up two bromine atoms rapidly and a third slowly ; hence it is best to add a slight excess of bromine and to back-titrate with arsenite.

The determination of ascorbic acid (vitamin C) is a matter of considerable importance in nutritional studies. One method in frequent use is by titration with 2 : 6—dichlorophenol-indophenol. A potentiometric method may be used to detect the end-point ;[39, 40] the " dead-stop end-point " method has also been shown to be applicable, since an excess of the reagent causes depolarisation of the electrodes, with consequent flow of current.[41]

A possible indication of the directions in which the " dead-stop end-point " method may develop is afforded by the work of Clippinger and Foulk.[42] They studied the addition of substances which they termed " electrometric indicators " to titrations in which an electrometric end-point is otherwise not given. The earliest example of the use of such a substance was studied by Willard and Fenwick[43] in connection with their electrode system. These workers found that the addition of hydrogen peroxide to acid or to alkaline solutions gave sharp, non-permanent end-points in neutralisation titrations.

Clippinger and Foulk showed that the addition of two drops of 3% alcoholic iodine solution enables an acid solution to be titrated with alkali. The added iodine acts as a cathode depolariser, while the first excess of alkali forms anodically-active iodide ions. In the titration of alkali with acid, a small amount of iodide-iodate solution is added to the former, thus causing anodic depolarisation by the iodide ions. As the titration proceeds, a trace of iodine (which depolarises the cathode) is liberated when the pH is slightly less than 7.

Nitrite, which depolarises the anode, may be added as electrometric indicator in the argentimetric titration of halides. A slight excess of silver depolarises the cathode, so that the sudden commencement of current flow signals the end-point in the usual manner.

32 Evans, D. P., and Simmons, N. T., *J.S.C.I.*, 1944, **63**, 29.
33 Evans, D. P., *Analyst*, 1947, **72**, 99.
34 Gluckauf, E., Heal, H. G., Martin, G. R., and Paneth, F. A., *J.C.S.*, 1944, 1.
35 Pagel, H. A., and Miers, J. C., *Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 334.
36 Pring, M. E., and Spencer, J. F, *Analyst*, 1930, **55**, 375.
37 Bratton, A. C., McClendon, J. F., Foster, W., and White, R., *Ind. Eng. Chem. Anal. Ed.*, 1938, **10**, 600.
38 Bielenberg, W., and Kuhn, K., *Z. anal. Chem.*, 1943, **126**, 88.
39 Becker, E., and Gleria, J. de, *Vitaminforschung*, 1937, **6**, 86.
40 Harris, L. J., Mapson, L. W., and Wang, Y. L., *Biochem. J.*, 1942, **36**, 183.
41 Liebmann, H., and Ayres, A. D., *Analyst*, 1945, **70**, 411.
42 Clippinger, D. R., and Foulk, C. W., *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 216.
43 Williard, H. H., and Fenwick, F., *J. Amer. Chem. Soc.*, 1923, **45**, 715.

Microchemistry Group of The Society of Public Analysists and other Analytical Chemists

The following office-bearers of the above Group were elected for 1948 at the Fourth Annual General Meeting : Chairman, Dr. Norman Strafford ; Vice-Chairman, Dr. Janet W. Matthews ; Hon. Secretary, Mr. Ronald Belcher ; Committee—Professor H. V. A. Briscoe, Dr. A. F. Colson, Mr. G. Ingram, Mr. D. F. Phillips, Mr. J. T. Stock, Mr. E. J. Vaughan.

Alloys made by Electric Ingot Process

By H. R. Clauser

AN electric ingot process has been developed by the M.W. Kellogg Company which is claimed to eliminate many of the defects common in steel produced by the usual means. It is a specialised process and for economic reasons is most applicable to the production of high quality, high cost alloys. At present it is being used chiefly for making high-speed tool steel, special types of stainless steel, and high-temperature alloys. Work has been done on high silicon and high aluminium metals, aeroplane exhaust valve steels, and special welding rod steels.

In this new process, material in strip form is fed through a tube mill, where it is formed into a continuous tube. This tube is fed down into a water-cooled ingot mould which is, in effect, an electric furnace with the tube serving as the electrode. The arc that is struck melts the metal in the mould. Another tube of smaller diameter extends part way down through the larger tube. This second tube is connected with a metering device which supplies predetermined amounts of the alloying ingredients and a flux to the system. The flux is sometimes added separately. The alloying ingredients and flux fall from the feeding tube into the arc and are melted along with the tube. The flux upon melting floats to the top and serves as a protective cover between the atmosphere and molten metal. A thin coating of flux also sticks to the sides of the mould and permits easy removal of the ingot.

Alloys made by the electric ingot process are of exceptionally high quality. Since all the raw materials are melted simultaneously right in the ingot mould, high uniformity of chemical composition throughout the ingot is attained. Segregation, shrinkage cavities and pipes, which are always present in the centre and upper portions of ingots made by conventional practice, are virtually eliminated. There are several reasons for this: (1) Solidification of the molten metal takes place rapidly because the mould is water-cooled. (2) The ingot solidifies by what might be termed "progressive solidification." Instead of the entire ingot being cast at once, only a relatively small volume of molten metal is present and solidifying at any one time. Thus, transfer of heat away from the liquid metal is much faster. (3) Liquid metal is fed continuously to the solidifying metal to compensate for shrinkage upon cooling. This feeding of molten metal continues to the very top of the ingot, so that the usual hot top is eliminated.

To illustrate the virtual elimination of segregation, a chemical analysis was made of a typical ingot of medium carbon, 12% chromium steel made by the electric ingot process. Samples were taken at top and bottom, outside and centre. The chemical analysis at these various points is given below.

	Top Centre	Top Outside	Bottom Centre	Bottom Outside
C	0·35	0·37	0·35	0·36
Mn	0·53	0·54	0·54	0·55
Si	0·36	0·36	0·36	0·36
Cr	12·5	12·7	12·8	12·9

In the field of high-temperature alloys, improvement in mechanical properties of materials made by this process is of special significance. The most striking advance is in ductility. High-temperature alloys are notoriously lacking in ductility, particularly when the specimens are taken from the central portion of forged turbine rotors. They generally have elongations varying from 0–10–15%.

As yet only a few high-temperature test results are available on electric ingot alloys. Several bars were taken from the central portion of a turbine rotor forging of 16-25-6 type alloy. These bars showed a stress to rupture life at 20 tons/sq. in. at 650° C. of 145 hr.

The processing characteristics of high-temperature alloys made by this process are in most respects the same as those made by conventional melting practice. In forging them, however, certain precautions must be taken to obtain their optimum properties. If normal forging procedures are used, forged billets from ingots made by conventional practice have better forgeability characteristics. The grain size in electric ingot alloys as-cast is larger than in the billets that have already had some work done upon them.

In commercial practice alloys made by this process have operated up to 650° C. and in experimental work, up to 780° C. Work is now in progress on developing new alloys, using this process, for temperatures of 815° C. and higher. At present gas turbine buckets are either precision cast or forged and then fastened to the rotor mechanically or by welding. Often the rotor and buckets are made of different materials. A possible future application of the electric ingot process will be to produce a composite ingot, the core of which will be of the rotor alloy, while the outer layer will be of the bucket alloy. The buckets could then be machined out of the rim material. This would eliminate the joining operation and also possibly eliminate the area of weakness now present at the joint.

This ability of producing composite ingots made up of two different alloys should open up many other fields of application where materials with different properties are desired in the same part.

One of the first uses to which the electric ingot process was put was for making high-speed tool steels. In tool and die steels an important consideration is the carbide segregation usually present at the centre of the ingot and in the subsequent bar stock. This segregation results in a brittle centre zone with low ductility and impact properties. Segregation is largely eliminated in electric ingot alloys and the brittle carbides instead

From *Materials and Methods*, 1948, Jan., 57–61.

of being concentrated at the centre are uniformly dispersed throughout the alloy, resulting in higher and more uniform properties.

An advantage of the process is that, where practical, tools and dies can be made directly from the cast ingot. An example of this is in the manufacture of milling cutters. The cutters vary in diameter from approximately 4–10 in., and the ingots are made to this size. They are then shaped from the ingot in the same fashion as are cutters made from forged high-speed steel bars.

All types of stainless steel can be made by the electric ingot process, but it probably will concentrate on applications where extra high quality is required or where special properties are needed. It has been found, for example, that the machinability of some types can be improved considerably by adding small amounts of lead which is uniformly dispersed through the alloy.

In summary then, the electric ingot process offers a new and unique method of producing alloys of extra high quality and uniformity. The most important applications of these alloys have been discussed and should give some idea of their present range of use. But the process is still new; there certainly will be further improvements and refinements which will probably result in more economical production, and thus make possible an even wider application of electric ingot ferrous and non-ferrous alloys.

Metallic Titanium

By E. A. Gee, J. R. Long and W. H. Waggaman

TITANIUM is the fourth most plentiful structural metal in the earth's crust, being exceeded by aluminium, iron and magnesium. It is light, strong, and resistant to corrosion, properties which are of great importance to designers and users of modern equipment, because of the ever increasing demand for light-weight, high-speed machines.

Up to the present time the main use for titanium minerals has been in the non-metallic field. Enormous quantities of the oxide are now used in paint, thus relieving the drain on our reserves of lead and zinc, which heretofore have been the basis of the paint industry. Pigments consisting chiefly of precipitated titanium dioxide are exceptionally white, have excellent covering power and little tendency to chalk or discolour when properly prepared. Other non-metallic uses for titanium are the manufacture of salts for the dyeing industry, for the production of titanium chloride, an unusually effective smoke screen material, for welding rod coatings, and in the production of titanium carbide which has proved very useful as a cutting tool.

Exploitation of titanium metal has lagged despite its exceptional properties and a plentiful supply of titanium-bearing minerals because the metal as initially produced was so contaminated with impurities that its true properties were not known, and because the difficulties encountered in preparing the pure metal were such as to discourage commercial development. Processes are now known by which the ductile metal can be readily and consistently produced, and at least one method has been shown to be applicable to large-scale production. Chemically, titanium is a very active metal and reacts readily with such elements as oxygen, nitrogen and carbon, forming hard compounds which embrittle the metal. Extreme care must, therefore, be taken to avoid contamination with these substances. Hydrogen also embrittles titanium, but this element, unlike the others, can be readily removed from the metal by vacuum treatment and, therefore, creates no difficulties.

Melting of titanium by conventional means has not been too successful. The molten metal dissolves, reduces, or reacts with all standard crucible materials such as zirconium, thoria, magnesia, calcium oxide, etc., and thereby becomes contaminated. The use of conventional powder metallurgy methods for bonding the material well below the melting point circumvents these difficulties. The clean granular titanium thus produced is pressed into compacts and sintered for 16 hr. under vacuum at a temperature of 1,000° C.; after this the metal can be rolled into bars and sheets by standard fabricating methods.

Experimental work has demonstrated that the metal can be successfully melted in an arc between tungsten electrodes, and ingots about 20 cu. in. in size have been prepared. The melting of titanium is one of the basic problems which must be surmounted if cheap metal is to be produced. Recent research on vacuum melting in graphite have shown some promise, and this technique is now under further investigation.

Considerable study is now being devoted to alloys of titanium with many other metals, but data concerning the desirable alloy combinations and resulting properties are not yet available. It is known, however, that titanium will readily alloy with many metals and that selected alloys will undoubtedly be amenable to heat-treatment in a manner similar to steel. It is too early to predict just what the investigations of the alloys of titanium will bring forth, but in the case of nearly every other metallic element this field of research has yielded products having physical and chemical properties superior in many respects to the metal alone. There is no reason to believe that alloys of titanium will prove an exception to this rule.

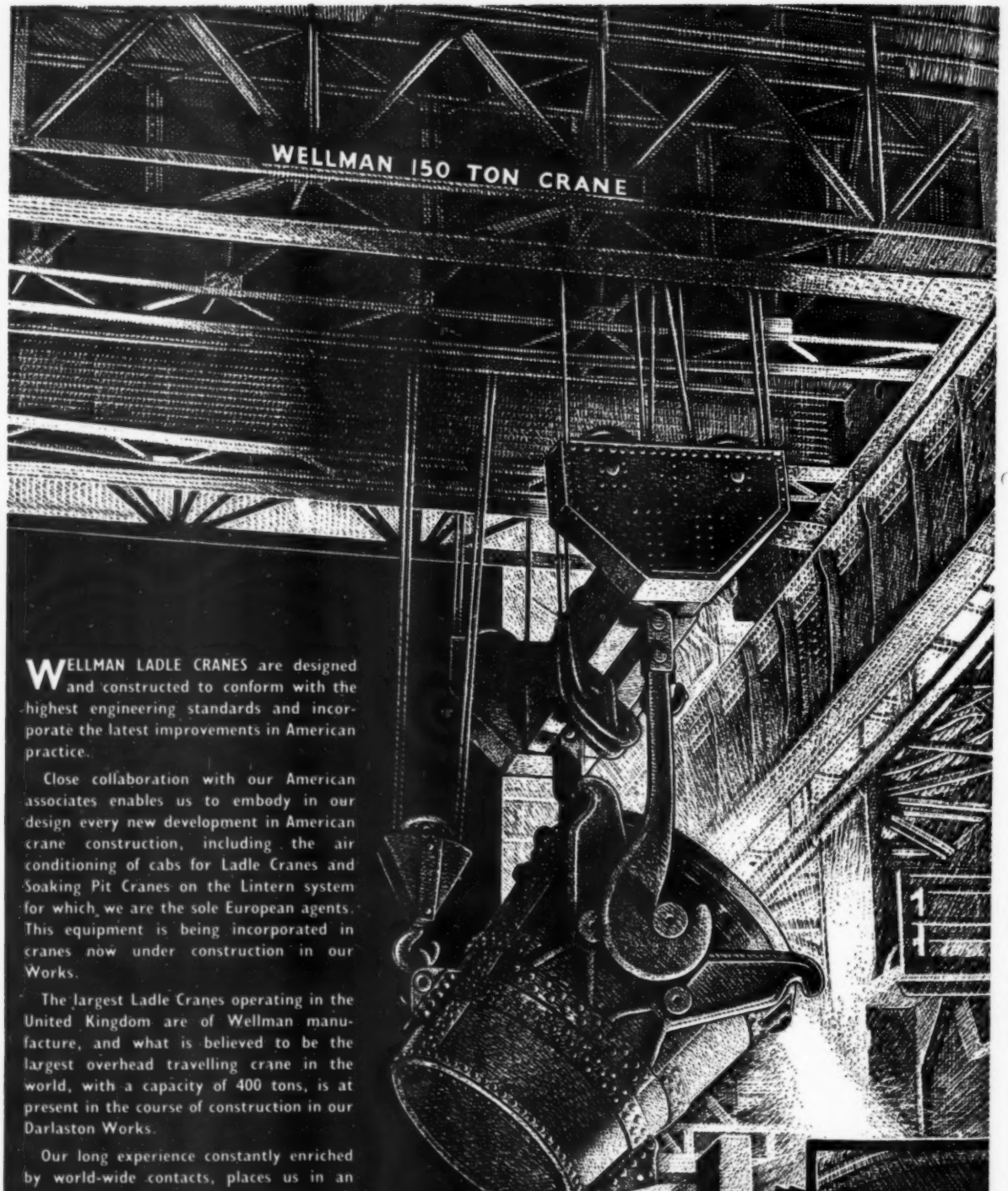
From *Materials and Methods*, 1948, Jan., 75-8.

Ceramic Coatings for High-Temperature Protection of Steel

A NEW type of ceramic coating for the protection of mild steels in high-temperature service, developed during the war, is described in the National Bureau of Standards research paper. Laboratory and service tests have shown this coating to be superior to conventional porcelain enamels for high-temperature service. The outstanding features of the coating are: (1) High resistance to chipping under repeated severe thermal shock; (2) protection of the metal against oxidation during prolonged exposure in air at temperatures up to about 680° C.; (3) freedom from cracking and blistering produced in conventional porcelain enamels under comparable conditions of high temperatures and severe thermal gradients; and (4) a mat surface that does not show highlights and, therefore, decrease the visibility.

To prepare these coatings, a mixture of a special grade of calcined aluminium oxide and a conventional type of ground-coat frit is ground with water to appropriate fineness and is then applied to the metal, dried, and fired according to well-known methods. The coatings may be used on low

From National Bureau of Standards, R.P. 1773, vol. 38, Mar., 1947.



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carbon steel in a thin application of only 0·002–0·003 in.

Specifications were issued by the U.S. armed services, and the coating was used in regular production during the war on a number of exhaust systems of aircraft and other vehicles, by both the Army and the Navy.

Shot Peening of Non-Ferrous Metals

By Harold A. Knight

DURING the war considerable experimental work with peening was organised by governmental technical services and probably about 10% of the materials experimented on were non-ferrous metals. In these studies consideration was given to material, hardness, intensity of peening, shot size, shot type and nature of surface before peening. In addition to peening, other pre-stressing processes were used such as surface rolling, hammer peening and pre-setting. Studies were also made of temperature effects on pre-stressed specimens of certain super alloys.

Among the non-ferrous metals, studies were chiefly on the effect of shot peening on fatigue strength and on stress corrosion cracking. Other tests dealt with the effect of peening on season cracking, crushing strength and static strength. Some fatigue durability tests gave the following results: Peening improved duralumin by 16%; magnesium alloy, Elektron AZ 31, gained 26%, with Elektron casting, 24% better. Phosphor-bronze wire improved 43% and sheet, 54%.

Certain aircraft domes of aluminium alloy forgings were peened inside and outside except the tapped hole at the top and clamping surface of the flange. Threads were cold-rolled with a special tool. Two domes were bolted together to form an assembled accumulator. Then cyclic hydraulic pressure was applied, 90 cycles per min. A non-peened dome failed at 89,200 cycles; a peened, at 121,000. The experimenters were evidently conservative when they said: "The limited data indicate that the component *may* be improved by peening."

An experimenter reported that shot-peening was beneficially applied to a machine part (a phosphor-bronze brake armature support diaphragm) as thin as 0·008–0·010 in. The shot used was commercial malleabilized iron, 0·016–0·019 in. dia. The shotpeening intensity was too low to measure with standard apparatus. Coverage was considered ample as judged by visual examination. The part, shaped somewhat like a quarter moon, but actually a strip ¼-in. wide, was peened all over.

From *Materials and Methods*, 1947, Nov., 83–5.

Another test involved a nose wheel torque collar of aluminium alloy. Critical areas and fillets were peened (the internal bearing surfaces and tapped holes being masked). The test or load was a laboratory fatigue similar to that given in service, applied pneumatically. The average durability of two shotpeened collars was 130% greater than those not peened.

An important purpose of shot-peening non-ferrous metals is to extend stress corrosion resistance. Thus, in cold-drawn brass (copper 68·6; zinc 31·3) cups, $\frac{1}{32}$ in. thick, and exposed after peening to an ammonia atmosphere, the time before cracking was extended to 23 hr. from 2½ hr. for non-peened brass, for one specimen and to 100 hr. for another.

In another instance where the brass cup was subjected to ammonia atmosphere, generated by 100 cc. of 75% ammonia hydroxide solution (by volume), the stress corrosion cracking life increased many times by peening both outside and inside surfaces. In the case of a large brass cartridge case it was observed that stress corrosion cracking was more effectively decreased by large shot at high intensity than by small shot at lower intensity.

Magnesium alloy (AMC-57 SH) test strips, when stressed and exposed to potassium chromate and sodium chloride, failed in 120 sec.; when peened, they lasted 10 days with no cracking or corrosion. J-7H magnesium alloy sheet failed in 9¼ min.; when peened it lasted 430 hr.

Another interesting series of experiments was conducted on Dow J-1H magnesium alloy sheet since this material is highly susceptible to stress corrosion in the as-received condition. Specimens were prepared from sheet, 0·064 in. thick. Strips 1 by 10 in. and 1 by 9 in. were stressed by bending into arcs with 8½-in. chords and held in this position during testing. The different length of specimens provided 2° of stress for observation of the effect produced by this variable.

An interesting application has been to cure porosity in aluminium die castings subjected to pneumatic or hydraulic pressures. In the case of one part leakage was reduced from 50% of all parts made to 20%; in another case from 16% formerly to 4% after peening. One maker of such die castings shotpeened on both sides of the casting in a rotary-type, multi-table machine. As a result 90% of the castings had no leakage, while 10% had only slight seepage.

The International Nickel Co. is experimenting with shotpeening of various nickel alloys. A novel use of peening is testing the silver adhesion to silver-plated steel bearings as practised at Pratt and Whitney Aircraft. The hammering action of the shot produces deformation of the silver. If the silver is poorly bonded it will extend and flow and become blistered. Several makers of aluminium cooking utensils have shot-peened for decorative purposes and also to resist corrosion pitting.

The Structure of Surfaces Polished Mechanically and Electrolytically

By H. Raether

USING electron-diffraction methods and the electron microscope the author has investigated the effect of polishing in relation to the structure of the metal surface and to the amorphous or finely crystalline structure of the resulting surface layer. The microgeometry of the surfaces was examined by means of the electron microscope using both the reflection method in which the electrons reflected from grazing incidence are focussed to give an image which reveals the asperities as dark shadows, and the transmission method in which a thin replica of the surface is made and a measure of the roughness of the surface is obtained by noting the variation in intensity of the rays transmitted through the replica. Diffraction patterns given by high-speed electrons were used to investigate the surface structure and with this method it was found possible to deduce the properties of a layer of thickness 10 A.

Work with thin films of gold and copper subjected to mechanical action showed that cold working results in a breaking-up of the crystalline structure. Reflection diagrams at different surface depths could be obtained by removing successive layers electrolytically. Monocrystals of copper were examined in this way. It was seen

From *Metaux et Corrosion*, 1947, **22**, pp. 2–17. Reproduced from *Light Metals Research*, **8**, No. 25, 615–6.

that in the upper layers the structure was destroyed by mechanical polishing whilst at greater depths the structure approached that of the undisturbed crystal.

Selenium and antimony crystals were used to determine whether the surface state, after mechanical polishing, is finely crystalline or amorphous, as the patterns for the two states are quite distinct in these two metals. Results showed that the surface is finely crystalline. The hardening effect of mechanical polishing and the tendency to return to the monocrystalline state are referred to and investigations carried out with ionic crystals are described.

The second part of the article deals with electrolytic polishing. The Jacquet process is considered to be important for the study of structure, for the polishing of parts inaccessible to mechanical action and for the production of perfectly plane surfaces. Using the collodion replica process in the electron microscope, an image almost without contrasts was obtained. Electron diffraction gave spectra which differed considerably from those obtained for mechanically polished surfaces and showed that electrolytic polishing removes the deformed surface layer and brings out the undisturbed structure. Chemical attack of the surface would also lead to this result, but in that case the surface would appear matt. It is concluded that electrolytic polishing results in a rounding of the angular profile of the initial surface.

All Carbon Blast Furnace Hearths

HARD-baked carbon hearths, each weighing nearly 260 tons, are being used in the two new blast furnaces which Carnegie-Illinois Steel Corporation is building at its South Chicago works, and another which has recently been rebuilt and blown in at Gary, Ind. All three furnaces will meet new, ultra-modern specifications of the United States Steel Corporation and soon each will be producing more than 1,500 tons of iron per day for use in the manufacture of steel.

The carbon hearth was specified because carbon is not adversely affected by temperatures ranging from 2,700°–3,000°F. common to the smelting of iron. Moreover, carbon expands less than most materials under great heat and is impervious to molten iron and slag. The standard hearth, which is built of big carbon blocks, is 33 ft. 6 in. in outside diameter. Its carbon bottom is 3 ft. 9 in. thick and the vertical sides, 2 ft. 3 in. thick, rise 9 ft. 4 in. to form the cup in which molten iron and slag will be collected.

Beneath the carbon hearth of each of these big furnaces is a still larger foundation cup of concrete, 58 ft. in diameter and 20 ft. high, extending 11½ ft. below and 8½ ft. above ground level. Between the carbon and the concrete cups are seven courses of high-quality refractory brick, totalling 10½ ft. in thickness, as well as 2 ft. 3 in. of second quality brick.

The body or "stack" of each of the three furnaces, as of practically all blast furnaces, is shaped roughly like the chimney of an old-fashioned kerosene lamp. But these stacks are 108 ft. high—a total of 205 ft. when charging and other overhead equipment is counted. Where a lamp chimney is glass, these are built of brick, 3 ft. 4½ in. thick for most of the height, enclosed in a welded steel shell. At the bulge above the hearth, where the heat is most intense, the brickwork is reduced to 2 ft. 3 in. thick but is water-cooled. Unlike a lamp chimney, the blast-furnace stacks are closed at the bottom, in this case by the carbon hearths, whose inside diameter approximates the width of a three-lane road.

For the three furnaces carbon blocks 22½ in. thick, 30 in. wide, and up to 15 ft. long for the hearth bottoms, and smaller blocks for the walls, were specified. These blocks were ordered made of a mixture of sized petroleum coke and low-ash anthracite which had been heated to drive off volatile matter. Mixed with pitch, they were extruded by a hydraulic press at 2,000 psi, then baked in sealed ovens at temperatures of 1,800°–2,000° F. for periods up to seven weeks.

The new carbon hearths are said to represent the last word in hearth construction. Although they cost considerably more than hearths made of brick, they are considered worth the difference. They are also reported to give greater protection to the men who operate the furnaces and to increase the quantity of iron that can be obtained from a furnace without interruption for repairs.

From *Mech. Eng.*, 1948, Jan., 21–2.

A Theory for Mechanism of Chromium Plating—A Theory for the Physical Characteristics of Chromium Plate

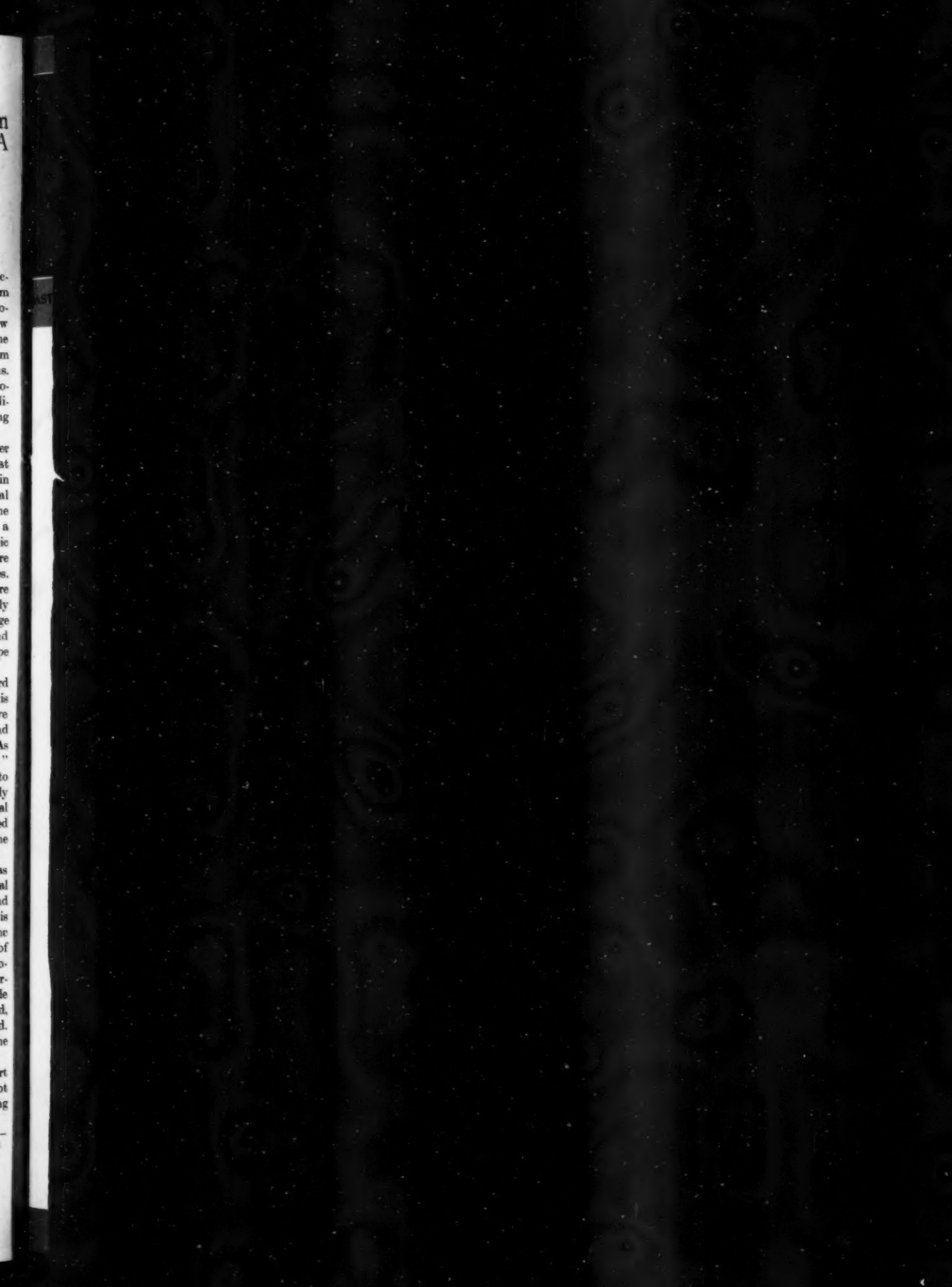
By Cloyd A. Snavely

A GENERAL study of the structural characteristics of chromium plate and of the mechanism of chromium plating is described. New fundamental data are presented on the crystal structure of chromium deposited from chromic acid solutions. In view of deposition conditions producing the various structural modifications, a hypothesis for the plating mechanism is presented.

Solution composition and other plating factors can be adjusted so that chromium deposits either as metal in the body-centred cubic (B.C.C.) crystal arrangement, as a hydride in the hexagonal arrangement, or as a hydride in the face-centred cubic arrangement. The hydrogen atoms are interstitially placed in the hydrides. The body-centred cubic plates are stable, but the hydrides are structurally unstable and decompose with shrinkage in volume to form B.C.C. metal and hydrogen. The hydrogen may escape or may be occluded in the plate.

It is postulated that the hard chromium plate of commerce is "cracked" because of successive deposition of hexagonal hydride and its decomposition during plating. As this cracking occurs, "cathode film" is drawn into the shrinkage cracks to fill them with a compound of partially reduced chromium. These physical effects, their magnitude, and the speed of their occurrence are governed by the cathode film.

The cathode film is postulated as consisting principally of a "colloidal membrane" of such compositon and disposition that its isoelectric point is within the pH range operative at the cathode surface. At the low end of this range, body-centred cubic chromium is deposited; in the intermediate pH levels, hexagonal hydride is deposited; and at the high end, face-centred cubic hydride is deposited. Between these limits, mixtures of the various structures occur.

X-ray data are presented to support the concept that the hydrides are not merely metallic chromium containing "dissolved" hydrogen.

From Advance Copy of Paper presented at 92nd Gen. Meeting of Electrochem. Soc., Oct., 1947.